UNIVERSITY OF ARIZONA
39001006991411

Arizona
University
Library

◆

Presented by

Dr. F. N. Guild

Digitized by the Internet Archive
in 2022 with funding from
Kahle/Austin Foundation

https://archive.org/details/generalchemistry0000harr

GENERAL CHEMISTRY

THE MACMILLAN COMPANY
NEW YORK · BOSTON · CHICAGO · DALLAS
ATLANTA · SAN FRANCISCO

MACMILLAN & CO., LIMITED
LONDON · BOMBAY · CALCUTTA
MELBOURNE

THE MACMILLAN CO. OF CANADA, LTD.
TORONTO

GENERAL CHEMISTRY

966

BY

HARRY N. HOLMES
PROFESSOR OF CHEMISTRY
IN OBERLIN COLLEGE

New York
THE MACMILLAN COMPANY
1921

All rights reserved

PRINTED IN THE UNITED STATES OF AMERICA

COPYRIGHT, 1921,
BY THE MACMILLAN COMPANY

Set up and electrotyped. Published September, 1921.

UNIVERSITY OF ARIZONA
540
H75g
LIBRARY

Press of J. J. Little & Ives Co.
New York

PREFACE

This book has been written from the viewpoint of the student and not to impress men who are already trained chemists. It is a text in the full teaching sense of the term, not a reference book.

Many legitimate devices for securing and holding the student's interest have been used. This is certainly justifiable, for no array of facts and theories, no matter how imposing, can be of much value unless the student is interested. The style adopted is far from pedantic; homely illustrations are not disdained. Chemistry for college Freshmen should receive very different treatment from chemistry for more advanced students.

The order of topics adopted has proved satisfactory in actual practice. Chlorine and hydrogen chloride are studied as early as Chapter IX because of the excellent drill they provide both in the classroom and in the laboratory. Treatment of the Periodic System is delayed until two good illustrations of its relationships (the halogens, and sulfur, selenium, and tellurium) have been discussed. After such preparation the Periodic System means something to the student.

The first chapter has been freed from much of the usual material that only serves to make the student wonder when "real chemistry" begins. The beginner is, at an early date, given the "tools of his trade" in the form of symbols, formulas, and equations.

Valence, a rather intangible topic to many students, when first presented, is given a clear introduction by an experiment for which we are indebted to Professor W. A. Noyes.

The treatment of Molecular and Atomic Weights has been simplified. It is most important that the logical development of this subject shall be convincing to the student.

No apology is offered for the introduction of an entire chapter on Colloid Chemistry. The growing importance of the subject and its natural relation to the subject of solutions give it a prominent place.

Most of the students in Freshman chemistry go no farther.

They have a right to at least two chapters on Organic Chemistry. Such a vast field cannot fairly be slighted in a course labeled "General Chemistry." Furthermore, the student is greatly benefited by the training in logic involved, and delighted by the close relation of the compounds of carbon to daily life.

The subject of equilibrium is introduced very early in a simple way and referred to frequently. However, the fuller treatment is left to Chapter XXIX, part of which is frankly a résumé of what has been given in different places before. Such examples of repetition as this are intentional. Some repetition is essential to forceful teaching.

Problems are interspersed where a specific point needs illustration — not left to the end of the chapter to be a mere afterthought in preparation of the lesson.

Numerous references are given to books and journal articles within the grasp of first-year students. The library habit is invaluable. "One-book" chemists never go far.

The Great War gave teachers an opportunity to show the relation between "dry" chemical properties or reactions and the fate of nations. This relation has been made a feature of the book.

Special acknowledgment should be given to Professor W. H. Chapin of Oberlin College for very great assistance in correcting the manuscript and for permission to use material from his own course. Among the others who offered valuable suggestions are Professor Stuart R. Brinkley of Yale University, Professor Arthur John Hopkins of Amherst College, Professor J. H. Walton of the University of Wisconsin, Professor Eugene C. Bingham of Lafayette College, Professor J. Pearce Mitchell of Leland Stanford University, Dr. Wilmot Metcalf of Oberlin, Professor Roy B. Davis of the University of the South (Sewanee), Associate Editor E. E. Thum of the Journal of Chemical and Metallurgical Engineering, Dr. Martin H. Fischer of the General Hospital, Cincinnati, and my colleagues, Professors Jas. C. McCullough and E. H. Cox. To Professor Hopkins special thanks are due for much of the material in the chapter on chromium and manganese.

Mr. E. C. Bischoff of Oberlin is responsible for most of the drawings. The Century Company kindly permits the use of the solubility table. For a few of the illustrations the author is indebted to the Warner Chemical Co., the McGraw-Hill Co., the Scientific American, the American Book Co., and the Permutit Co.

Most of all I wish to pay tribute to the Dean of American teachers of chemistry, Ira Remsen, to whose admirable precept and example I owe whatever soundness there may be in this volume. In preparing the text I have also been greatly influenced by the excellent books of Alexander Smith, Cady, McCoy and Terry, Mellor, McPherson and Henderson, and Hildebrand.

HARRY N. HOLMES.

OBERLIN COLLEGE, 1921.

CONTENTS

CHAPTER PAGE

I. INTRODUCTION . . . 1

II. OXYGEN AND OZONE . . . 13

III. THE PROPERTIES OF GASES AND THE THREE STATES OF MATTER . . . 33

IV. HYDROGEN . . . 44

V. VALENCE . . . 59

VI. WATER AND HYDROGEN PEROXIDE . . . 65

VII. MOLECULAR AND ATOMIC WEIGHTS . . . 78

VIII. SOLUTIONS . . . 86

IX. CHLORINE AND HYDROGEN CHLORIDE . . . 103

X. BROMINE, IODINE, FLUORINE, AND THE HALOGEN ACIDS . 117

XI. THE OXYGEN ACIDS OF THE HALOGENS . . . 127

XII. IONIZATION . . . 137

XIII. APPLICATIONS OF THE IONIC THEORY . . . 147

XIV. SULFUR AND HYDROGEN SULFIDE . . . 161

XV. SULFURIC ACID AND THE OXIDES OF SULFUR . . . 175

XVI. SELENIUM AND TELLURIUM. THE PERIODIC SYSTEM . . 189

XVII. THE ATMOSPHERE. THE ARGON FAMILY . . . 205

XVIII. NITROGEN AND AMMONIA . . . 217

XIX. NITRIC ACID AND THE OXIDES OF NITROGEN . . . 233

XX. THE PHOSPHORUS GROUP . . . 250

XXI. CARBON . . . 277

XXII. THE HYDROCARBONS . . . 295

XXIII. DERIVATIVES OF THE HYDROCARBONS . . . 314

XXIV. SILICON AND BORON . . . 336

XXV. COLLOID CHEMISTRY . . . 346

XXVI. THE METALS . . . 361

XXVII. THE ALKALI METALS . . . 370

XXVIII. THE ALKALINE EARTH METALS . . . 396

XXIX. EQUILIBRIUM . . . 413

CHAPTER PAGE
XXX. Copper, Silver, and Gold 424
XXXI. Glucinum, Magnesium, Zinc, Cadmium, Mercury . . 441
XXXII. Electrochemistry 459
XXXIII. Aluminum and the Rare Earths 466
XXXIV. Tin and Lead 481
XXXV. Vanadium, Molybdenum, Tungsten, and Uranium. Radioactivity 497
XXXVI. Chromium and Manganese 510
XXXVII. Iron, Cobalt, and Nickel 525
XXXVIII. The Platinum Metals 544

Appendix:

Metric and English Unit Equivalents; Pressure of Water Vapor; Weight of 1 Liter of Various Gases 549
The Periodic Table. 550

Index 551

GENERAL CHEMISTRY

GENERAL CHEMISTRY

CHAPTER I

INTRODUCTION

Chemistry and Physics. — Chemistry treats of the composition and changes in composition of substances. It is also concerned with their properties and their energy relations.

Physics is largely a study of the various forms of energy such as light, heat, electricity, sound, mechanical energy, etc., while chemistry deals more with matter. However, each science is forced to include both matter and energy in its field.

Matter and Energy. — By *matter* is meant anything that occupies space or has mass (measured as weight). *Energy* is anything which can do work. The relation between energy and matter is very close. For example, chemical energy is stored up in dynamite and may be released as very active motion in all surrounding material. In a less exciting manner, we may release as heat the chemical energy stored up in coal — and are sincerely thankful for the phenomenon. When a given portion of matter changes its composition, energy may be released as light, heat, electricity, or motion; and conversely, these forms of energy may be applied to a portion of matter, forcing a change in composition. Heating limestone in the kiln changes it into lime and carbon dioxide. Light reduces the sensitive silver bromide on a photographic plate, and light also causes the carpet and the preserved fruits and vegetables to fade. A sharp blow decomposes nitroglycerine, although, to be exact, it merely starts the process. Infinitely more energy is released than is accounted for by the sharp blow. Electricity decomposes silver salts in solution, depositing metallic silver on objects to be plated.

Substances. — A body is an object, a definite portion of material, such as a bottle, a kettle, a stove or a statue. A substance is a particular *kind* of material such as gold, sugar, common salt, or sulfur. A bottle may be shaped from the substance glass, a kettle from the substance copper, a stove from the substance iron, and a statue from the substance marble; yet the same glass could be shaped into a kettle or statue, and the marble into a bottle. Evidently, then, shape and size do not identify glass, although they may well serve in classifying bottles.

Elements. — Substances that we can decompose into two or more simpler substances are called ***compounds***. Limestone is a compound substance because on heating in the limekiln it breaks down into quicklime and carbon dioxide. Red mercuric oxide on being heated decomposes into the colorless gas oxygen and the metal mercury. Hence both limestone and mercuric oxide are compounds. There are about two hundred and fifty thousand known compounds. There are also nearly ninety substances that have *not yet* been decomposed into simpler substances. These we call ***elements***. Familiar examples are iron, copper, oxygen, gold, mercury, sulfur and carbon. About ten of the elements are gases, mercury and bromine are liquids, and the rest are solids.

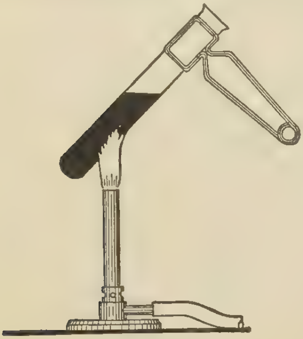


Fig. 1

Although nearly ninety elements are known, many of them are unusual. Oxygen makes up one half the known crust of the earth and silicon one fourth. The composition of the land, ocean, and air, as we know them, is estimated to be as follows:

	Per Cent		Per Cent		Per Cent
Oxygen	49.78	Calcium	3.19	Hydrogen	0.95
Silicon	26.08	Sodium	2.33	Titanium	0.37
Aluminum	7.34	Potassium	2.28	Chlorine	0.21
Iron	4.11	Magnesium	2.24	Carbon	0.19
					99.07

The other seventy-six elements make up the remaining one per cent of the earth's crust. The great majority of chemists have never seen nor worked with all the elements: in fact some of the elements are mere curiosities with no known use. But there is always the exciting possibility that the museum specimen of to-day may become of invaluable service to the world to-morrow: How short a time it has been since tungsten was of little consequence and radium unknown! Tellurium is useless now, although reasonably plentiful, but who can predict its future?

Exercise 1. — Common clay is an aluminum ore. Why does this metal cost much more than iron although more abundant in the earth?

Properties. — We identify different substances by certain characteristics called properties. Bodies are recognized by such properties as size and shape, for example, bottles and spoons, which may be of wood, glass, iron, etc. But substances must be identified by other properties. We must know whether a given substance is a solid, liquid, or gas at ordinary room temperature. The temperature must also be specified, since water, for example, may be solid ice, liquid water, or steam at different temperatures.

Then to identify substances completely we want to know the color, odor, taste, hardness, crystalline form, melting point, boiling point, solubility in water or other solvents, ability to conduct electricity, index of refraction and other properties. We may even ask if the given substance burns in the air. The student readily recognizes sulfur as such because it is a yellow solid, found in nature in rhombic crystals, melting at about 115° C., insoluble in water but soluble in carbon disulfide. If still undecided he burns it in the air, notes the blue flame, and throws aside all doubts after one breath of the choking gas formed. In recognizing lead a student is particularly interested in its softness and its low melting point. Sugar he knows at once by its sweet taste, although indiscriminate tasting is not to be recommended. Hydrogen sulfide once smelled is never forgotten and never separated from the thought of rotten eggs. In fact we pay money for specific properties of substances. Copper would not sell for fifteen or twenty cents a pound to the amount of over a million tons yearly if it were not such an excellent conductor of electricity. Obviously if glass were opaque or if it dissolved readily in water it would have a very limited market for use as window panes.

Exercise 2. — How do you recognize copper, lead, wood, salt?

Changes. — When a platinum wire is highly heated only a few properties change. Instead of the usual silver white, the color changes to red as the temperature rises but the hot platinum differs in very few respects from cold platinum. Moreover, on cooling all of its accustomed properties are resumed. A physical change took place.

If pure white sugar be heated to a high temperature it turns black and gives off steam. The black cinder left no longer tastes sweet nor will it dissolve in water. In fact nearly all the properties of the sugar have changed. The student cannot mix the steam and the black cinder (carbon) with any prospect of combining them into the sugar from whence they came. The change was chemical and hopelessly permanent.

A ***physical change*** in a substance involves very few properties, no change in composition, and is temporary in the sense that when the conditions producing the change are removed (temperature, pressure, etc.) the original properties are all regained.

A ***chemical change*** is usually permanent, in a sense, involving all or nearly all the properties. There is, consequently, a change in identity of the substance. The composition is usually altered and energy changes are involved.

Exercise 3. — Give a few illustrations of physical and chemical changes.

Pure Substances and the Law of Definite Composition.[1] — The percentage composition by weight of a given *pure substance* is always the same. Water from any portion of the earth, *if pure*, is composed of hydrogen and oxygen in the proportion of 1 part of hydrogen to 7.94 parts of oxygen by weight. If other elements are present they represent impurities and can readily be separated from the water. Any mixture of alcohol and water might look like water, but it would not be a pure substance. Incidentally it would not boil at 100° under 760 mm. pressure as does water, nor would it act chemically towards other substances exactly as does water. Sugar and clean white sand might be mixed very deceptively, but the analysis would show a very different composition from sugar. Such a material would not be a pure substance. If the sand were removed (How could you do it?), the remaining sugar would have the same percentage of carbon, hydrogen and oxygen as any other specimen of pure sugar.

The difference between pure compounds and mechanical mixtures is evident from this ***Law of Definite Composition.*** The proportions in any mechanical mixture may be varied considerably, as in the sand-sugar material, but if the proportions of carbon, hydrogen and oxygen in pure sugar were changed the substance would no longer be sugar. As a matter of fact, alcohol is composed of the very same elements as sugar and can be made from it, but the percentage composition is different. Thousands of pure substances contain only these three elements, but in each case either the proportions or the arrangement are different.

---

[1] Often called the *Law of Definite Proportions.*

A classic illustration of the difference between a mechanical mixture and a chemical compound is found in an experiment with iron and sulfur. If very fine iron filings be mixed with flowers of sulfur, it may be shown that the sulfur still retains its own characteristic properties as does the iron, and that each may be removed by simple mechanical means. A magnet attracts the iron as if the sulfur were not present. Carbon disulfide dissolves the sulfur out of the mixture as if the iron were not present and, on filtration, a clear solution (the filtrate) is obtained. This yields the sulfur if allowed to evaporate.

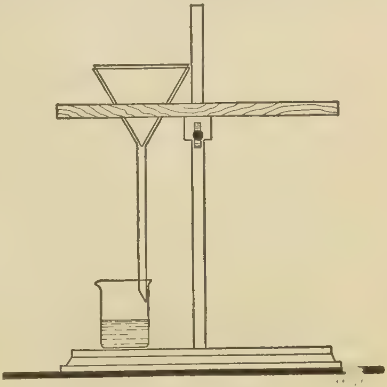


FIG. 2

If the mixture of iron and sulfur be heated in a test tube, interesting color changes are observed. Finally the mixture glows brightly, even after it is removed from the flame. Evidently heat is given off by some sort of action between the two elements. On breaking the tube a black solid is obtained which is not attracted by the magnet and from which sulfur is not dissolved by carbon disulfide. The conclusion is that neither free iron nor free sulfur is present, but that they have combined to form a compound. A reaction took place which when well started gave off considerable heat.

The experiment goes as described if the two elements are taken in one very definite proportion. If more iron than is called for by that proportion is used, some free iron is left over. If more sulfur than is called for is used, some sulfur is left over. The hard black solid obtained in the above experiment is a compound called iron sulfide. It has several properties quite different from those of iron or sulfur.

EXERCISE 4. — Is granite a mixture or compound? Brass? Flour? Iron rust? Iron ore?

Combining Weights.— If hydrogen be burned in oxygen, water is formed. A record of the weights of the gases used up shows that approximately 8 grams of oxygen unite with 1 gram of hydrogen to form water; in other words they combine in the proportion of 8 to 1. Now if 1 gram of hydrogen be united with sulfur, it will combine with exactly 16 grams to form hydrogen sulfide gas. Therefore we may speak of the combining weights of oxygen, sulfur, and hydrogen as 8, 16 and 1. The following table shows the relative weights in which several elements combine.

1 part Hydrogen combines with 8 parts Oxygen
1 “ “ “ “ 35.5 parts Chlorine
1 “ “ “ “ 3 parts Carbon
1 “ “ “ “ 16 parts Sulfur
8 parts Oxygen combine with 1 part Hydrogen
8 “ “ “ “ 3 parts Carbon
8 “ “ “ “ 23 parts Sodium
8 “ “ “ “ 9 parts Aluminum
35.5 “ Chlorine combine with 8 parts Oxygen
35.5 “ “ “ “ 23 parts Sodium
35.5 “ “ “ “ 20 parts Calcium
35.5 “ “ “ “ 9 parts Aluminum

From this a list of Combining Weights might be derived as follows:

Hydrogen = 1
Oxygen = 8
Chlorine = 35.5
Carbon = 3
Sulfur = 16
Sodium = 23
Calcium = 20
Aluminum = 9

100 g. of mercury unite with 8 g. of oxygen to form red mercuric oxide and 35.5 g. of chlorine also unite with 8 g. of oxygen. It might safely be assumed, then, that if they have any inclination to combine at all 100 gr. of mercury would combine with 55.5 g. of chlorine. Such is the case. This reminds us of the axiom that "things equal to the same thing are equal to each other."

A corollary to the above is the fact that 100 g. of mercury also unite with 2 x 35.5 g. of chlorine. In other words, some elements unite in different proportions by weight. When they do this, however, they form different compounds. This is true of hydrogen and oxygen, sodium and oxygen, iron and chlorine, and many other elements.

It is proper now to speak of the combining (or equivalent) weight of any element as the number of grams of that element that combine with 8 g. of oxygen or 1 g. of hydrogen or displace 1 g. of hydrogen. Since there are instances where two elements combine in different proportions, we may suspect that it is possible for one element to have two combining weights. This is true, but in such cases the weights of the one element uniting with the same fixed weight of the other are in the proportion of small whole numbers. (*Law of Multiple Proportions.*) For example, in water 8 g. of oxygen have united with 1 g. of hydrogen and in hydrogen peroxide 16 g. of oxygen have united with 1 g. of hydrogen. The ratio of 16: 8 is expressed by a simple integer, 2.

In the laboratory these values may be determined by synthesizing (building up) compounds with an accurate record of all weights involved or analyzing (tearing down) compounds with a similar record of weights. For example, the student may weigh out black copper oxide in a small porcelain boat and, after placing the boat in a hard glass tube, pass dried hydrogen gas through the tube while heating (Fig. 3). The hydrogen unites with all the oxygen of the copper oxide, leaving red copper. The steam formed is driven out by the steady stream of hydrogen. From the original weight of the copper oxide and the final weight of the copper one can, by simple subtraction, learn the weight of oxygen. An illustration follows:

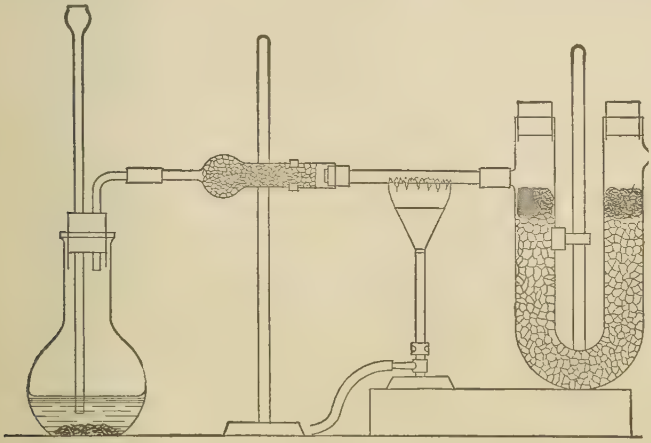


FIG. 3

Weight of boat+copper oxide	=4.178 g.
Weight of boat alone	=2.058 g.
Weight of copper oxide	=2.120 g.

Weight of boat+copper (after action) =3.758 g.
Weight of boat alone =2.058 g.

Weight of copper =1.700 g.

Weight of copper oxide =2.120 g.
Weight of copper alone =1.700 g.

Weight of oxygen =0.420 g.

Exercise 5. — Since the oxygen and hydrogen escape as steam, could you determine by the above experiment how many grams of hydrogen combine with 8 g. of oxygen?

Evidently 1.700 g. of copper combined with 0.420 g. of oxygen, as may be learned by subtracting the weight of the copper from the weight of copper oxide. To learn how many grams of copper would combine with exactly 8 g. of oxygen at this rate, we write a proportion.

1.70 g. copper : 0.420 g. oxygen :: x g. copper : 8 g. oxygen

Solving, $x = 32$ g.

Therefore the combining (or equivalent) weight of copper is 32 (approximately).

It is difficult to make metals unite with hydrogen, but most metals will displace hydrogen from acids. The number of grams of any metal — zinc, for example — that can take the place of 1 g. of hydrogen in an acid is certainly equivalent to the 1 g. of hydrogen, for it is combining with the rest of the compound just as did the 1 g. of hydrogen. For example, 32.7 g. of zinc displaces 1 g. of hydrogen from acids.

Atomic Weights. — For reasons to be explained soon (Chapter VII) we represent the relative weights of the elements taking part in reactions by atomic weights. These resemble combining weights and indeed they are either the same or, at most, small multiples of the combining or equivalent weights.

Element	Equivalent Weight	Atomic Weight
Oxygen	8	16
Copper	31.8	63.6
Hydrogen	1.008	1.008
Chlorine	35.45	35.45
Carbon	3.00	12.00
Sodium	23.00	23.00
Aluminum	9	27.00

The Atomic Theory. — A little over a century ago John Dalton, an English school teacher, sought an explanation for the facts described by the laws of definite composition and of combining weights. His theory declared that elements are composed of minute particles which he called atoms, all those of the same kind being alike in properties and weights but quite different from the atoms of other elements. Extending the theory we may believe that compounds are formed by the union of atoms of different elements. The smallest particles of such compounds, having all the properties of the compounds, we call ***molecules.*** The smallest particles of elements that take part in chemical reactions we call ***atoms.*** A reaction between two substances, then, means a regrouping of the atoms in new combinations.

This theory explains why, during a reaction between substances in a closed vessel, there is neither gain nor loss of weight (*Conservation of Mass*). All the atoms of the reacting substances are accounted for in the new substances.

It explains also the law of *Definite Composition.* Thus if it be true that when one element unites with another the combination always takes place between a definite number of each kind of atoms, then the resulting compound must necessarily have a definite composition. For example, if two atoms of hydrogen unite with one atom of oxygen to form water, and if an oxygen atom weighs, say, 16 times as much as a hydrogen atom, it surely follows that the percentage of oxygen and hydrogen by weight in pure water is always the same.

It also explains the law of *Multiple Proportion.* When two atoms of hydrogen unite with *two* atoms of oxygen (instead of one), we should have a new compound quite different from water. Such a compound is known under the name of hydrogen peroxide.

The numbers called combining weights are proportionate to the masses of the atoms reacting. The fact that some elements have more than one combining number is accounted for on the supposition that atoms combine in different ratios, as do lead and oxygen.

The atomic theory has been of enormous value in the development of chemistry. For a century it served as a good working hypothesis without any absolute proof of its correctness, but recently through studies in Radioactivity we have obtained convincing evidence of the existence of atoms and molecules and have even counted and weighed them. Millikan reports the number of molecules in a cubic centimeter of any gas under standard conditions as 2.71 x 10^{19}.

Symbols and Formulas. — Up to the time of Berzelius, about a century ago, chemists used strange symbols for the elements. The moon ☾ represented silver, ▽ was the symbol for water, ♀ stood for copper, and 🜍 for sulfur. But these were supplanted by Berzelius' suggestion that one or two significant letters of the name of the element be used. Thus the symbol for carbon is C, for copper Cu, for chlorine Cl, for calcium Ca, and for cobalt Co. To avoid confusion Ag (from the Latin *argentum*) was taken as the symbol for silver because S had already been selected for sulfur and Si for silicon. Fe for iron is taken from the Latin *ferrum*, Na for sodium from *natrium*, Pb for lead from *plumbum*, and K for potassium from *kalium*. According to our present conception symbols stand not only for the elements but for definite weights of the elements. For example, H represents a single atom of hydrogen and it is commonly used to mean the atomic weight in grams, that is, one gram. O means either a single atom of oxygen or 16 g. of oxygen.

To represent the formula of a compound we simply join the symbols of the constituent elements together and attach small sub-figures to represent the actual numbers of atoms in each molecule. H_2O as a formula for water tells us that two atoms of hydrogen and one atom of oxygen make up a single molecule of water. The weight of the whole molecule, 18, is of course the sum of the weights of all the atoms in it. H_2SO_4, as a formula for sulfuric acid, tells us that a molecule of the acid contains two atoms of hydrogen, one of sulfur and four of oxygen. The formula weight is 98 g. (How do we compute it?) The formula O_2 for the substance oxygen tells us that there are two oxygen atoms in each molecule.

A comparison of the formulas for sodium chloride, $NaCl$, calcium chloride, $CaCl_2$, and aluminum chloride, $AlCl_3$, shows us that although one atom of aluminum can hold in combination three atoms of chlorine, one atom of calcium can hold only two atoms of chlorine and an atom of sodium only one atom of chlorine. This holding power, which we shall later study as Valence, differs for different elements.

Equations. — With the use of symbols and formulas we can now represent chemical changes (reactions) very simply and clearly. For example, the equation[1]

$$CuO+H_2 \rightarrow H_2O+Cu$$

tells us that one molecular weight of copper oxide reacts with one molecular weight of hydrogen to form one molecular weight of water and one of copper. The weight of one molecule of CuO is obviously the sum of the weights of all the atoms in it. $Cu=63.57$ and $O=16$. Therefore $CuO=79.57$. The weight of $H_2=2$, of $H_2O=2+16$, or 18, and of $Cu=63.57$.

It is a very useful practice to consider these weights as expressed in grams. Of course the relative values are just the same whether expressed in the minute units of atomic weights, or grams, or tons. Expressed in grams we should read the equation thus:

79.57 g. copper oxide + 2.016 g. hydrogen react to form 18 g. water + 63.57 g. copper.

These so-called equations name the reacting substances and their products. "Balancing the equations" consists in prefixing such numbers before the molecular formulas as indicate the relative number of molecules concerned. Suppose the student knows by *laboratory observation* that hydrogen reacts with hot iron oxide to form iron and steam. He would represent this reaction tentatively by merely writing down the formula thus:

$$H_2+Fe_3O_4 \rightarrow Fe+H_2O.$$

but not *all* the atoms in the reacting substances are found in the products. After all, such a reaction is merely a regrouping of the elements in new combinations, so the student must account for all the atoms. There must be an *equal* number of H atoms on both sides, of Fe atoms, and of O atoms also. So the student begins with the most intricate formula and decides to try *one* molecule of Fe_3O_4. We do not prefix "1" to molecules; it is understood if no number is given. As a result of deciding to try balancing with one Fe_3O_4, we must account for three atoms of Fe on the right-hand side of the equation. Making this change, the equation will improve:

$$H_2+Fe_3O_4 \rightarrow 3\ Fe+H_2O.$$

It is evident that the four oxygen atoms in the Fe_3O_4 molecule are not all found in a single molecule of H_2O. It must require 4 H_2O to dispose of them. So we make another improvement:

---

[1] It used to be the universal custom to represent such a reaction thus: $CuO+2\ H=H_2O+Cu$, hence the name "equation."

$$H_2+Fe_3O_4 \rightarrow 3\ Fe+4\ H_2O.$$

But to write 4 H_2O on the right side requires that we place 8 atoms of hydrogen on the left or there will be no equality:[1]

$$4\ H_2+Fe_3O_4 \rightarrow 3\ Fe+4\ H_2O.$$

Now every atom is accounted for on both sides and we have not done violence to the inner structure of any compound nor have we represented anything that was not produced in the laboratory. The equation is, therefore, properly "balanced."

A chemical equation, then, must represent the reacting substances, the products formed and the relative weights involved. It does not, however, name the conditions necessary — temperature, etc. — to cause the reaction to take place, nor does it tell how rapidly it occurs nor to what extent the reaction occurs.

Determination of Formula from Analysis. — Suppose analysis showed a compound to contain 27.06 per cent of sodium, 16.47 per cent of nitrogen, and 56.47 per cent of oxygen. What is the formula of the compound?

In 100 g. of compound	Atomic weights in grams	Number of gram atomic weights of each element in 100 g. of compound
27.06 g. sodium	Na = 23 g.	$27.06 \div 23 = 1.176$ g. sodium
16.47 g. nitrogen	N = 14 g.	$16.47 \div 14 = 1.176$ g. nitrogen
56.47 g. oxygen	O = 16 g.	$56.47 \div 16 = 3.528$ g. oxygen

This ratio between the number of gram atomic weights of the three elements present, 1.176 : 1.176 : 3.528, may be written 1 : 1 : 3. Hence there is in each molecule one atom of sodium, one atom of nitrogen and three atoms of oxygen, and the formula is $NaNO_3$. Of course this ratio would hold if the molecule were two or three times as heavy, but it is best to accept the simplest formula. Later we shall learn how to determine the weight of each molecule and to apply that knowledge to the determination of formulas.

Exercise 6. — A certain compound contains, by analysis, 29.40 per cent of calcium (Ca), 23.56 per cent of sulfur (S), and 47.04 per cent of oxygen. What is its formula?

---

[1] Had we been unable to "strike a balance" using one Fe_3O_4, we could then have tried 2 Fe_3O_4, 3 Fe_3O_4, etc.

CHAPTER II

OXYGEN AND OZONE

OXYGEN

History. — The history of modern chemistry begins with the discovery of oxygen, the most important element. In 1774 Priestley, an English clergyman, heated a number of different substances resting on the mercury in inverted glass tubes. The source of heat was the sun's rays concentrated by a lens a foot in diameter. On heating red mercuric oxide a gas was evolved in which a splinter burned far more brilliantly than in air. Furthermore, a mouse became much more active in this gas than in air. Priestley named the gas "dephlogisticated air." It was produced from the mercuric oxide as represented by the equation:

$$2\ HgO \rightarrow 2\ Hg + O_2.$$

A year earlier Scheele, a brilliant but poverty-stricken drug clerk in Sweden, obtained oxygen by heating manganese dioxide, potassium nitrate and five other substances. Priestley published his results first, but both men deserve credit as independent discoverers.

Lavoisier, a celebrated Frenchman, sometimes called the "father of modern chemistry," at once applied himself to a systematic study of the new substance, and by a convincing experiment showed its relation to air. He heated mercury in a retort (Fig. 4) for twelve days and then observed a red powder formed on the surface of the mercury. The end of the retort dipped under a jar in a larger dish of mercury, so the volume of the air in the retort was definitely known. During the heating this volume decreased one fifth and the gas left in the retort extinguished a burning splinter. On heating the red powder to a still higher temperature

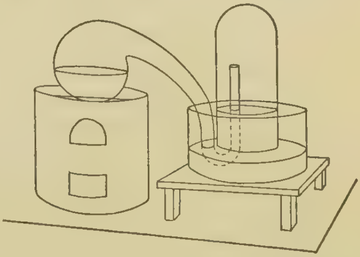


FIG. 4

a volume of gas was given off exactly equal to the loss in volume of the retort air. Moreover this evolved gas possessed all the properties of Priestley's "dephlogisticated air." Lavoisier named it "oxygen," from the Greek word for "acid-producer," because he thought it was contained in all acids, a mistake on his part. But he was right in his conclusion that oxygen was an essential part of air.

To be historically correct we must admit the probability that the Chinese had known for centuries of an active element in air which united with sulfur and other elements. A few Europeans also knew something of this element before Priestley, but he really began a great chapter in the study of oxygen.

Lavoisier's experiment cleared up the current uncertain ideas of combustion and rusting, for he had calcined or rusted mercury, showing that it united with oxygen from the air to form an ash, mercuric oxide.

Exercise 1. — From some good history of chemistry (Moore, published by McGraw Hill Co., is excellent) learn later incidents in the lives of Priestley and of Lavoisier.

Occurrence. — Oxygen makes up one half of all matter that we know. Two thirds of the human body is combined oxygen. Water contains 89 per cent, ordinary clay, sand, limestone and granite about 50 per cent. One fifth of the air is oxygen, the other four fifths nitrogen. This is the only occurrence of free oxygen. Elsewhere it is found in compounds.

Preparation. — 1 The most natural source of oxygen is the air where it occurs free but mixed with nitrogen, from which it is not easily separated. The separation is accomplished by liquefying air and then allowing it to evaporate. The more volatile nitrogen escapes first, leaving the oxygen, which is pumped into strong steel cylinders at 100 atmospheres pressure. The gas thus obtained naturally contains a little nitrogen, which does no harm for commercial uses. This modern process is now the only commercial method used on a large scale. The nitrogen also has a ready market.

2. The electrolysis of water releases hydrogen at the cathode and oxygen at the anode. This process is used commercially to some extent because the product is very pure and because there is a good demand for the hydrogen. The cost is too great for it to compete with the liquid air process.

3. The laboratory methods, where convenience is more important than cheapness, in most cases consist in heating oxygen compounds. It is possible to follow Priestley and heat mercuric oxide:

$$2\,HgO \rightarrow 2\,Hg + O_2.$$

The mercury is volatilized and condenses in a mirror or in drops on the cooler parts of the tube.

We may emulate Scheele and heat potassium nitrate:

$$2\,KNO_3 \rightarrow 2\,KNO_2 + O_2.$$

Only a third of the oxygen is driven off and potassium nitrite remains.

Manganese dioxide on being heated very hot gives off only part of its oxygen:

$$3\,MnO_2 \rightarrow Mn_3O_4 + O_2.$$

Barium dioxide releases just half its oxygen when sufficiently heated:

$$2\,BaO_2 \rightarrow 2\,BaO + O_2.$$

In fact this was the basis of the Brin process, once the chief commercial method. Barium oxide was heated in the air at 500° C.:

$$2\,BaO + O_2 \rightarrow 2\,BaO_2.$$

At this temperature the monoxide united with more oxygen to form the dioxide, although at 800° C. and higher the BaO_2 could be decomposed, reversing the action. By the clever device of lowering the pressure considerably and keeping the temperature constant at 700° C. the barium dioxide released half its oxygen. The barium oxide, on increasing the pressure of air, again became the dioxide at the same temperature and the process was repeated *ad infinitum*.

Potassium chlorate melts at 351° C. and at about 400° C. releases oxygen:[1]

$$2\,KClO_3 \rightarrow 2\,KCl + 3\,O_2.$$

If into a test tube partly filled with melted potassium chlorate which is giving off very little oxygen we drop a mere pinch of powdered manganese dioxide, there is at once an enormous increase in the rate of evolution of the gas. Potassium chlorate alone does not give off oxygen much below 400° C., yet in the presence of manganese dioxide the gas is rapidly released at 200° C. This is the basis of the usual laboratory method. No exact amount of manganese dioxide is needed. About one fourth as much as the weight of the potassium chlorate is satisfactory. The manganese dioxide aids the reaction and is called a "catalyst" (see page 27). In Fig. 5 and Fig. 6 are represented the usual laboratory methods

---

[1] In reality $KClO_4$ is first formed and this at higher temperatures gives up all its oxygen.

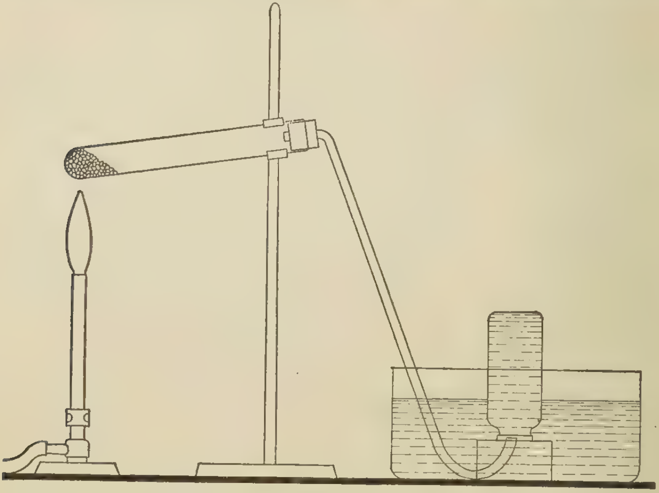


FIG. 5

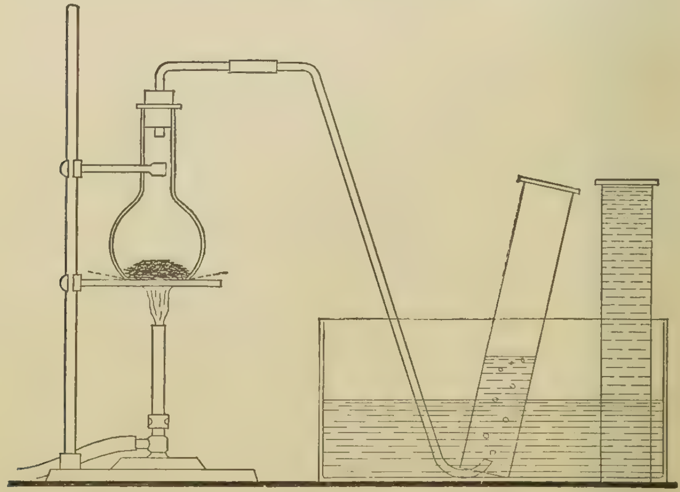


FIG. 6

of preparing oxygen in quantity. The oxygen evolved from the heated mixture of potassium chlorate and manganese dioxide is collected by displacement of water, in which it is but slightly soluble.

4. Sodium peroxide (made by heating sodium in air) reacts with water to form oxygen and sodium hydroxide:

$$2\ Na_2O_2 + 2\ H_2O \rightarrow 4\ NaOH + O_2.$$

This is expensive but very convenient, as the water may be allowed to drop slowly from a dropping funnel on the peroxide, releasing oxygen as needed.

Physical Properties. — It is important to have a record of the physical and chemical properties of the elements and compounds, but the student is not asked to burden his memory beyond reason.

Oxygen is a colorless, odorless, tasteless gas which is 1.105 times as heavy as air. One liter weighs 1.429 g. measured at 0° C. and a barometric pressure of 760 mm. It may be liquefied at and below −118° C., but no pressure is great enough to compress it to a liquid above −118° which may then be called its ***critical temperature.*** At this critical temperature 50 atmospheres pressure are required to liquefy oxygen; hence this is the ***critical pressure.***

Liquid oxygen is light blue, boiling at −182.5° under atmospheric pressure. It is attracted to a magnet just like a bar of iron. Dewar froze oxygen to a pale blue, snowlike solid, melting at −227°.

Oxygen is slightly soluble in water. At 20° and 760 mm. pressure 100 cc. of water dissolves 3 cc. of oxygen. Curiously enough it dissolves in molten silver, 10 cc. in 100 cc. of the silver.

Chemical Properties. — Oxygen is only moderately active chemically at ordinary temperatures, but at elevated temperatures it unites with every element except fluorine and a few rare and inactive gases. It is true that sodium rapidly oxidizes at room temperature but iron rusts slowly and carbon is attached very slightly indeed.

If the metal sodium be heated and then placed in a jar of oxygen, it burns brilliantly with a yellow flame. The only possible reaction is the direct combination of the two elements forming sodium oxide or, to be exact, sodium peroxide:

$$2\ Na + O_2 \rightarrow Na_2O_2.$$

Calcium burns almost as brilliantly, forming ordinary quicklime or calcium oxide:

$$2\ Ca + O_2 \rightarrow 2\ CaO.$$

Sulfur, first ignited with a flame, also burns with far greater vigor in oxygen than in air, forming sulfur dioxide:

$$S + O_2 \rightarrow SO_2.$$

The experiment with carbon is best performed with a stick of charcoal, which can be held in the forceps. After igniting it in the Bunsen flame, it is thrust into a jar of oxygen, where, instead of merely glowing, it bursts into flame. Pure carbon burns without flame:

$$C + O_2 \rightarrow CO_2.$$

It seems incredible, but iron in the form of steel wool or picture wire will burn in oxygen if first heated red hot. It may be necessary to dip the end of the wire into sulfur as a sort of match head. Dazzling sparks (Fig. 7) fly in all directions, and drops of molten iron often break the glass bottles. Water in the jar may save the glass:

$$3\ Fe + 2\ O_2 \rightarrow Fe_3O_4.$$

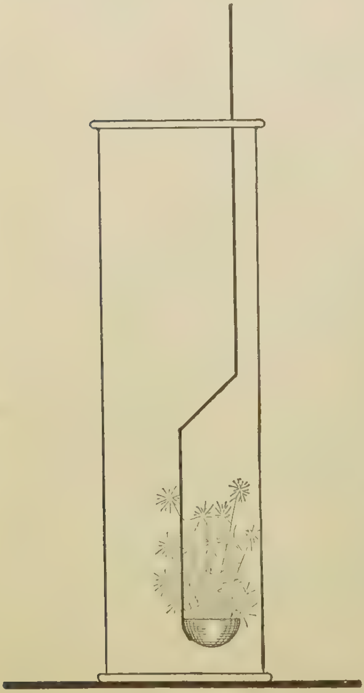


Fig. 7

Having formed these various oxides, add a little pure water to each jar, cover with a glass plate or cork, and shake.

Into each jar throw a small piece of blue litmus paper and one of red. The water on the sodium oxide turns red litmus blue, as does the calcium oxide water. Both waters feel soapy to the touch. The sulfur dioxide water turns blue litmus red as does the carbon dioxide water. The effect of the iron oxide water is too slight to be detected. These oxides have reacted with water in two ways, some to form bases which turn red litmus blue and some to form acids which turn blue litmus red. Elements whose oxides react with water to form bases are called *metals* and elements whose oxides react with water to form acids are called *non-metals.*

$$2\ Na_2O_2 + 2\ H_2O \rightarrow 4\ NaOH + O_2$$
$$CaO + H_2O \rightarrow Ca(OH)_2$$
$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$

The products above are called sodium hydroxide, calcium hydroxide, sulfurous acid and carbonic acid, respectively.

Oxides. — An oxide is a compound of oxygen with one other element. Water is an oxide of hydrogen. Potassium chlorate is not an oxide, for it contains more than two elements. Most oxides can be made by direct combination of oxygen with one other element, but a few elements like gold and platinum must be led into such union by indirect methods. Many oxides are made conveniently by heating carbonates, nitrates, and hydroxides. Quicklime is an example:

$$CaCO_3 \rightarrow CaO + CO_2.$$

Exercise 2. — Air is a mixture of nitrogen and oxygen. When nitrogen unites with all the oxygen it can take on directly the product is a poisonous, corrosive reddish-brown gas. Now have you any reason to think that the reaction

$$N_2 + 2\ O_2 \rightarrow 2\ NO_2$$

occurs when air is heated? We may ask this question again when nitrogen is studied.

Combustion. — When substances react heat is usually (but not always) liberated. If the reaction becomes so vigorous that light is also produced it is called combustion. As a rule this term is applied to a union of oxygen with other substances, but many other reactions produce light. The burning of fuel in a furnace is a common example of combustion. We sometimes speak of the ***kindling temperature*** as the temperature at which a given substance in contact with air bursts into flame. This is not a very definite temperature, however, as it may vary with the relative amount of surface of the substance, with the pressure of the air, and with the presence of other substances (see catalysis) that aid reactions. For example, iron can be made in a powder so fine that on exposure to the air it bursts into flame. Many substances will not burn in oxygen or air, but that may be because they already contain all the oxygen they can hold.

Phlogiston. — Becher, and later Stahl (1723), sought to explain combustion by assuming the escape of a sort of volatile spirit called *phlogiston!* Indeed the upward rush of flame gives some such impression. The ash of wood no longer burned because it had lost all of its phlogiston. A splinter ceased to burn in a limited volume of air because the air became filled with phlogiston and could take no more. Combustible substances were those that contained phlogiston and their burning was merely the escape of this mysterious spirit. Jean Rey annoyed the phlogistonists when in 1630 he weighed a metal before and after heating in air and showed that the ash or "calx" weighed *more* than the metal (Fig. 8). The theory of the escape of something from the metal on burning called for a *loss* in weight. So tenacious and blinded were the followers of the theory that they explained Rey's experiment by insisting that phlogiston had negative gravity.

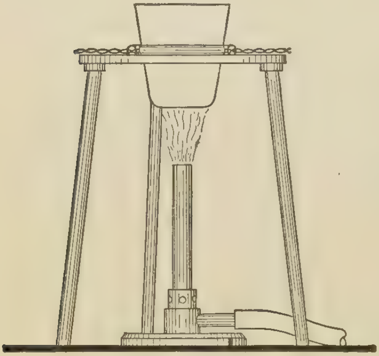


Fig. 8

Lavoisier's famous experiment (1777) of heating mercury in a definite quantity of air and then reheating the mercuric oxid formed and securing a volume of oxygen exactly equal to the loss in volume of air sounded the death knell of the phlogiston theory. This experiment showed that the increase in weight which occurs during oxidation is equal to the weight of oxygen absorbed from the air. For half a century the ablest minds of the world believed in phlogiston and the great Priestley died unconvinced by Lavoisier's explanation of combustion.

Exercise 3. — Why does the ash of wood or coal weigh less than the original fuel while the ash of heated metals weighs more?

In Fig. 9 is represented a candle placed directly under an open tube filled with sticks of sodium hydroxide, all balanced by weights on the other pan of the balance. When the candle is lighted the pan on the left sinks. The increase in weight is due to the fact that oxygen of the air unites with the wax of the candle and to the additional fact that the gaseous products of combustion are caught by the sodium hydroxide.

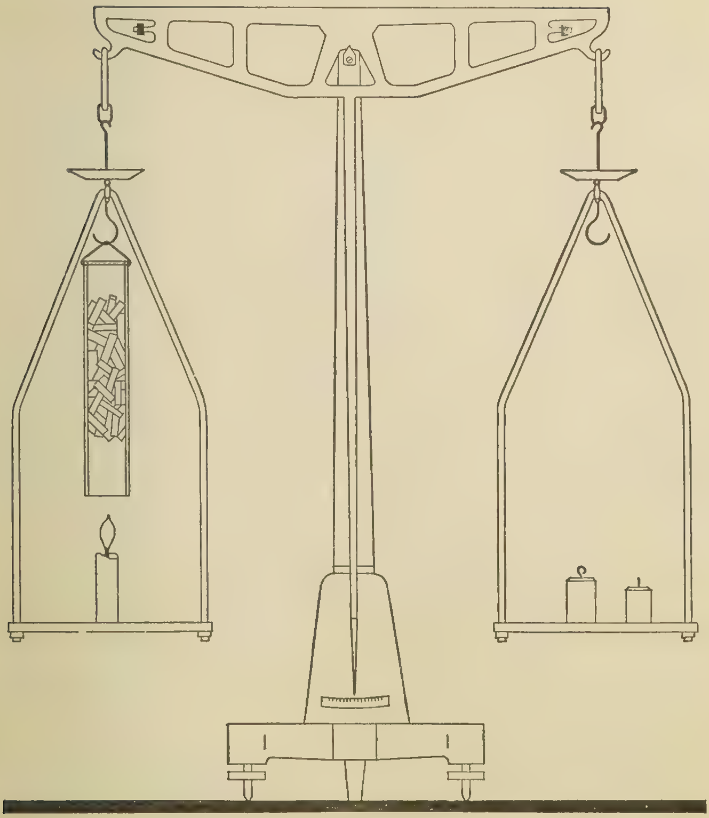


FIG. 9

Heat of Combustion. — Reactions accompanied by the evolution of heat are *exothermic* and those that require the application of external heat to sustain them are *endothermic.* To measure this heat we use the calorie as a unit. A calorie is the amount of heat required to raise the temperature of one gram of water one degree (at 15° C.). The large calorie (Cal.) is one thousand times as great.

The heat of combustion of any pure substance is the number of calories liberated when the formula weight (molecular weight in grams) is burned. For example, a molecule of carbon monoxide weighs 28, hence its formula weight is 28 g. When 28 g. of this gas burns it liberates 68,200 calories and becomes carbon dioxide.

The following table gives the heat of combustion of several substances:

SUBSTANCE	FORMULA WEIGHT	HEAT OF COMBUSTION
Carbon	$C = 12$ g.	97600 calories
Sulfur	$S = 32$ g.	70400 calories
Hydrogen . . .	$H_2 = 22$ g.	68800 calories
Carbon monoxide .	$CO = 28$ g.	68200 calories

EXERCISE 4. — How much heat is liberated when 136 g. of sulfur burns? When 24 g. of carbon burns to CO_2?

Engineers quite commonly refer to British Thermal Units, B. T. U., instead of calories. This B. T. U. is the amount of heat required to raise one pound of water 1° F. Since 1 lb. = 453 g. and 1° F. = $^5/_9$ of 1° C., it is evident that 1 B. T. U. = 252 calories. Very good soft coal may yield 15,000 B. T. U. per pound.

EXERCISE 5. — A ton of coal with a B. T. U. value of 14,560 per pound will raise the temperature of how many liters of water 40°?

EXERCISE 6. — Calculate the number of calories in one British Thermal Unit.

The *bomb calorimeter* is the apparatus in which we burn solids to measure their heat of combustion. This apparatus consists of a strong metallic *bomb*, gas-tight. A weighed amount of a solid to be burned is placed in the bomb, which is filled with oxygen under high pressure (to secure better combustion). The bomb is surrounded by a known amount of water contained in a vessel well insulated against heat loss.

A wire is heated by a current of electricity so as to ignite the substance. From the weight of water and its rise in temperature as well as similar data for the calorimeter itself we can accurately compute the total number of calories evolved.

Oxidation. — The union of oxygen with a substance is called oxidation. (Later we shall find some other reactions also included under that term.) Oxidation may be so slow that no light is evolved and very little if any rise in temperature noticed. As a matter of fact when a gram of any substance oxidizes slowly it liberates exactly the same quantity of heat as when it burns violently. In slow oxidation heat is usually conducted away so rapidly that a rise in temperature is not noticed. The rusting (slow oxidation) or burning of metals (rapid oxidation) is illustrated by the following equations:

$$2\,Mg + O_2 \rightarrow 2\,MgO.$$

The change from "hard" cider to vinegar is a union of alcohol of the cider with oxygen of the air to form acetic acid. The "mother of vinegar" is an organism that aids this reaction.

The animal body is a wonderful apparatus for the oxidation of food. The oxygen of the air meets the blood in the lungs and combines with the bluish hemoglobin of venous blood to form red oxyhemoglobin of arterial blood. This oxyhemoglobin is taken through the smallest capillaries and gives its oxygen to the wornout tissues of the body, burning them into carbon dioxide and water for the greater part. Carbon dioxide is exhaled from the lungs. The heat of this oxidation maintains the animal temperature and is approximately equal to the heat evolved when the same food is burned rapidly in a calorimeter. In other words the animal's body is both furnace and engine for the conversion of the chemical energy of food into heat and motion.

Ordinary decay is a slow oxidation brought about by the aid of minute organisms. City sewage dumped into a river is oxidized by oxygen dissolved in the water. Harmless and inoffensive products result. Life without oxygen would be not merely intolerable but impossible.

The "drying" of paint is not the loss of water but the oxidation of linseed oil to form a tough solid that is no longer sticky.

Exercise 7. — The Eskimos eat more fat than we do. What do you assume about the relative fuel values of fat and your own usual diet?

Spontaneous Combustion. — If the heat from a slow oxidation is not conducted away fast enough it may accumulate, finally bringing the temperature of the substance to the ignition point. This is *spontaneous combustion.* Coal oxidizes on storing and a loss of several per cent occurs. Usually the circulation of air between the lumps is sufficient to conduct this heat away, but large heaps of poor coal containing a good deal of fine material sometimes rise in temperature to actual combustion. Such fires are difficult to put out and the aggregate loss is enormous. Some air circulation, but not too much, is necessary to develop trouble.

The possible remedies are the replacement of air by an inert gas (not practicable yet) or the use of ventilation pipes to remove heated air. In the tropics coal has been stored under water in order to exclude air, but this practice has its drawbacks.

Waste rags soaked in oils, like linseed, which oxidize readily, are very likely to ignite spontaneously. It is safer to dispose of such oily waste or to keep it in closed tin cans.

The occasional explosions in coal mines, flour mills, and factories where there is much fine combustible dust are not to be blamed on spontaneous combustion. Flour dust, for example, when suspended in the air, is in excellent contact with oxygen. A spark from the machinery may produce combustion so rapid as to be explosive. This explosion throws more dust in the air, making matters worse. In a coal mine gas explosions are often followed by dust explosions. Coal dust on the ledges fills the air after the first explosion. In factories the remedy is to keep down the dust and to "ground" all machinery likely to develop sparks of frictional electricity. In the summer of 1919 factory dust explosions in the United States caused a loss of 70 lives and 7 million dollars' worth of property.

Exercise 8. — Would the explosion risk in a coal mine be lessened if heavy rock dust were frequently scattered on the floor and ledges? Why?

Uses of Oxygen. — Oxygen is the most useful element. Essential to animal life in burning out waste tissue and furnishing heat, beneficent in its disposal of sewage and other waste matters that would otherwise be a nuisance and a menace to health, vital in developing heat, light and power from fuel — it is, in short, the central element. Oxygen, compressed in steel cylinders, is used for the oxyhydrogen (or oxyacetylene) torch. This is a burner by which hydrogen or acetylene is burned in pure oxygen instead of in air. The extremely hot flame produced cuts through iron (by melting and burning the iron) like a knife. The transportation of scrap iron occurring in the inconvenient form of bridges, boilers, etc., is tremendously aided by cutting it into smaller sections with the oxyacetylene torch. Again the localized high temperatures are convenient in "autogenous welding." Unfortunately the oxyacetylene flame has been of great help to burglars in opening safes.

A rather small quantity of oxygen is used in medicine to revive weakened patients and to administer with nitrous oxide ("laughing gas") when the latter is used as an anesthetic. Nitrous oxide alone would cause suffocation. Oxygen is also needed in submarines and caisson tunneling to replace that used up by the workman.

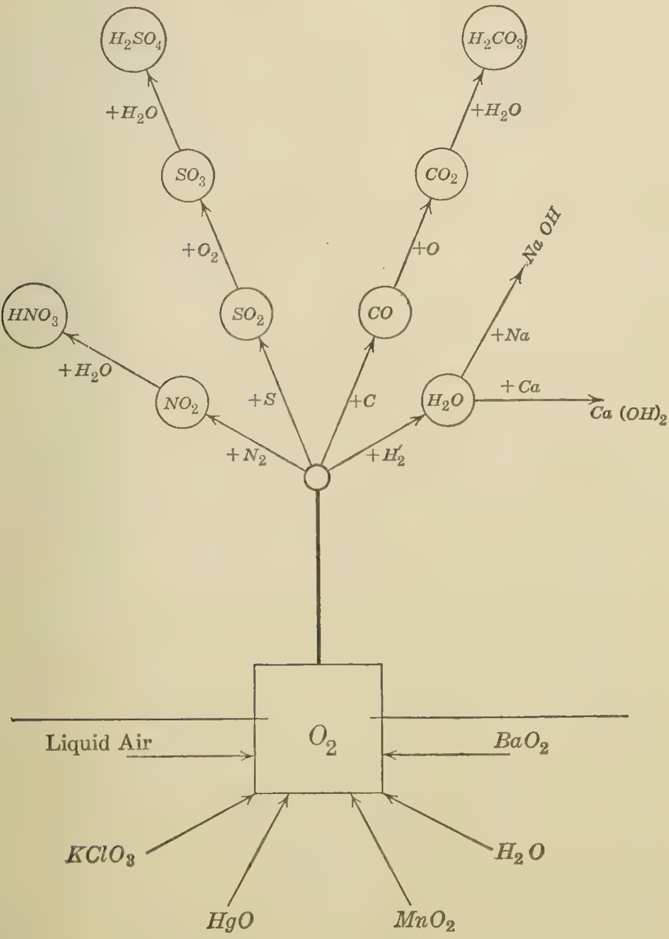


FIG. 10

Industry is impatiently waiting for a cheap process of separating oxygen from the nitrogen of air. When that is achieved blast furnaces for making iron from ores will be operated with a blast of oxygen instead of air. For every ton of pig iron made five tons of air are required.. The possibility of increased efficiency here is attractive.

Influencing the Speed of Reaction. — The speed of chemical reactions is greatly influenced by temperature, by the concentration of the reacting substances, by the presence of catalysts and by the amount of contact surface.

A rise in temperature of 10° doubles or trebles the speed of most reactions. This is understood when we remember that a rise in temperature means that the molecules move faster, consequently hit each other harder and oftener. Reactions probably continue at low temperatures but at rates too slow to observe. This temperature influence is familiar in cooking. In a pressure cooker with the steam retained by a tight lid tough meat is made tender at perhaps 125° in a fraction of the time required in an open vessel where the temperature would be little more than 100°.

The concentration of two substances thoroughly mixed also affects speed of reaction. It can be expressed quite simply in the phrase "opportunities for contact." If, for example, in a cubic centimeter there are one million molecules of A and one million of B, the reaction takes place at a definite speed. Now if the concentrations of A be doubled, two million molecules in the cubic centimeter, it is obvious that the opportunities for contact between A and B will be doubled, that is, the speed of reaction will be doubled. If at the same time the concentration of B increase to three million molecules per cubic centimeter, the velocity of reaction must increase to 2×3 or 6 times. Charcoal and other combustibles burn more brilliantly in pure oxygen than in air because only one fifth of air is oxygen, therefore, pure oxygen at the same pressure has five times the *effective* concentration of air. Furthermore, much of the heat produced is absorbed in raising the temperature of the useless nitrogen.

With two substances that cannot be mixed thoroughly, such as a solid and a gas, the amount of surface of the solid is of great importance. Splinters or shavings burn much faster than a thick log — a matter of "opportunities for contact." Coal dust is now blown into cement kilns with air and burned like a spray of oil.

Each dust particle is in such good contact with air that combustion is rapid, and very high temperatures are attained. In fact the flame is almost too hot for ordinary boilers. In the case of a solid and liquid mixture stirring speeds up reaction by bringing fresh molecules to the surface of the solid.

A ***catalyst*** is a substance that aids or retards a reaction without itself being permanently changed. Some catalysts condense the reacting substances on their surface, thus bringing in the influence of increased concentration. In cigar lighters the vapors of methyl alcohol mixed with air pass over a thin platinum wire. There is a little oxidation without the platinum, but with increased concentration on the platinum surface the heat of oxidation makes the wire incandescent, igniting the alcohol. Gas lighters are much the same. Other catalysts enter into reaction but are released in their original form by further reactions. Manganese dioxide aids the release of oxygen from potassium chlorate at 200° by reacting to form a compound that decomposes readily, releasing oxygen and the original manganese dioxide. It is evident that a very little of a catalyst can be used many times over, almost indefinitely, in fact. Platinum powder is an invaluable commercial catalyst, for by its aid sulfur dioxide is rapidly oxidized:

$$2\ SO_2 + O_2 \rightarrow 2\ SO_3.$$

The trioxide formed readily reacts with water to form sulfuric acid. Also nitrogen and hydrogen unite at a profitable rate with the help of uranium or other catalyst:

$$N_2 + 3\ H_2 \rightarrow 2\ NH_3.$$

Since ammonia (NH_3) is valuable in making fertilizers and is easily oxidized by the further use of platinum as a catalyst to nitric acid, it is plain that catalysis is not a mere theoretical subject.

OZONE

History. — Van Marum (1785) observed a peculiar odor near an electrostatic machine. Cruikshank (1801) noticed the same pungent odor in oxygen freshly made by the electrolysis of water, but failed to explain it. Schoenbein named the odor "ozone" (Greek "to smell"), but not until 1865 was its real nature discovered by Soret.

Occurrence. — There has been much argument as to the existence of traces of ozone in the air. Many writers repeat the original antique statement that the only times when perceptible quantities are found are during and immediately after a thunderstorm. Undoubtedly the lightning flash does generate a little ozone, but in the warm and moist air characteristic of thunderstorms ozone is quickly destroyed. It has been shown conclusively (American Chemical Journal, Vol. 47, 497, 1912) that the atmosphere contains the most ozone not in summer but in winter. High barometric areas, which are merely whirling mountains of air, throw the upper air to the earth's surface faster than under any other conditions. As a result the ozone formed a few miles up by the ultraviolet rays of the sun reaches the surface before it is all destroyed by heat, dust and other agencies. Air is not very permeable to ultraviolet light and so the action of these rays from the sun is greatest in the upper layers. Cold, dry and dustfree, the upper air gives a favorable environment for the existence of ozone. The stimulating effects of cold, "bracing" weather, when a "high" barometric area is passing over us, are due *in part* to ozone. We must be careful, however, not to overstate the benefits. Unscrupulous advertisers of health resorts often make extravagant claims.

Properties. — Ozone is a gas 1.5 times as heavy as oxygen, colorless, of a pungent odor, somewhat soluble in water and very soluble in turpentine, bluish when liquefied, and far more active chemically than oxygen. It even oxidizes silver if catalyzed by a trace of silver oxide. Ozone is rather explosive when highly compressed or liquefied. It is unstable at high temperatures, turning into oxygen. Three volumes of oxygen yield only two volumes of ozone and on decomposing (when heated above 280° C., for example) are changed back to the three volumes of oxygen. The evidence cannot all be given until later, but we might as well look ahead in the book a little and learn now that oxygen gas contains two atoms to the molecule while ozone contains three of the same atoms. The change from oxygen to ozone is expressed thus:—

$$3\ O_2 \leftrightarrows 2\ O_3.$$

When ozone oxidizes any substance it usually does so with the third atom, releasing a molecule of oxygen. Thus:

$$H_2S + O_3 \rightarrow H_2O + S + O_2.$$

Preparation. — Although made in nature chiefly by the ultraviolet rays of the sun, ozone is produced in the laboratory and on a commercial scale by the silent electric discharge. When two plates of glass or other insulating material are placed parallel and close together with metal plates against the *outer* side of each, we have a simple ozone machine. An electric current will jump across the gap between plates *if* the potential or voltage is high enough. This high voltage is secured by the use of an induction coil. In the same way if a short section be removed from a water pipe the stream of water will jump the gap if the pressure of water is sufficiently great. Without the broad insulating plates the electricity would jump in the form of sparks, but with adequate insulating plates the discharge is "silent." In a darkened room a bluish glow is seen. If air or oxygen is passing between the plates some of the oxygen is transformed into ozone. A commercial ozonizer is made of a number of pairs of plates. For the laboratory two concentric tubes with tin foil on the inside of the smaller and on the outside of the larger may be made to serve very well (Fig. 11).

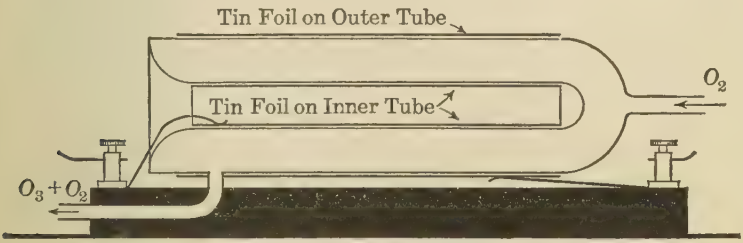


FIG. 11

Since heat and the electric discharge decompose ozone into oxygen, it is the best economy to blow the ozonized air away with a fan.

At very high temperature oxygen changes into ozone, but so rapidly does the heat decompose the product that it is only by the most rapid cooling that any ozone can be detected. In this case heat energy is taken up while in the commercial ozonizer it is electric energy. It is no wonder, then, that ozone is more active than oxygen; it contains more energy. A gram of carbon burned in ozone thus releases more heat than a gram of carbon burned in oxygen. This additional heat comes from the decomposition of ozone.

$$3\ O_2 \leftrightarrows 2\ O_3$$

This equation shows that each substance changes into the other and yet explains how ozone can be both made and decomposed by high temperatures. Warburg states that at 16° C. 1% ozonized oxygen decomposes in 1.7 minutes; at 100° in 0.003 miuutes, and at 1000° almost instantaneously.

A simple laboratory method of preparing ozone is to drop concentrated sulfuric acid on barium peroxide. It is best to smell this cautiously because too much ozone is irritating. Possibly also a spray of minute drops of the acid may add to the irritation. Passing the gas through a loose wad of cotton or glass wool would catch any spray.

Fluorine reacts so violently with water that the oxygen released contains 14 per cent of ozone.

In general it is probable that whenever anything unites with oxygen, even at high temperatures , or whenever oxygen is released from a compound, some ozone is formed, although usually decomposed instantly. The release of separate atoms of oxygen gives a chance for them to unite in twos or threes to form O_2 or O_3, oxygen or ozone. If a stick of moist white phosphorus be placed in a stoppered bottle of air (with some water in the bottle) ozone can be smelled, and can be detected in other ways. In fact it is said that the odor of unburned matches is the odor of ozone caused by the slow oxidation of phosphorus in the match. If a red-hot wire be plunged into a jar containing vapors of ether, ozone is formed, due to the slow oxidation of ether.

It has already been mentioned that electrolytic oxygen contains ozone. With dilute sulphuric acid of 1.1 density as electrolyte, as much as 17.23 per cent of ozone has been secured at very small, cooled anodes.

Uses. — Ozone is used to sterilize water, to purify indoor air, to sterilize bandages, etc., in hospitals, to bleach oils, flour, delicate fabrics and in a few oxidation processes in chemical manufacture. It is easy to overstate these uses. Its only extensive application to-day is in killing bacteria in city water that has first been settled and filtered. Even this use has been largely a European affair.

Over a hundred foreign cities treat their water supplies in this way with success.

In air treatment it is not probable that bacteria are killed, for a concentration fatal to bacteria would prove very irritating to people. But ozone oxidizes the warm and moist organic matter of human breath, "air sewage" as it is called, and thus prevents the decay of such material into depressing poisons. Odors also are oxidized into harmless substances. It has been stated that a low concentration of ozone stimulates the nerves regulating respiration and circulation.

On all this there is much difference of opinion. Perhaps ozone may find a legitimate use in oxidizing odors in restaurants, kitchens and food warehouses.

Tests. — Some authorities claim to smell one part of ozone in 10,000,000 parts of air, rivaling hunting dogs in keenness. A simple test is the development of blue color in a starch-potassium iodide paper:

$$O_3 + 2\ KI + H_2O \rightarrow O_2 + I_2 + 2\ KOH.$$

Ozone releases free iodine, which then turns blue on contact with starch. Unfortunately any good oxidizing agent such as nitric acid or hydrogen peroxide will do this. But if the gas to be tested is slowly passed through a tube heated above 280° C., any ozone would be destroyed. This serves as a check on the test. Mentzel used "tetramethyl base" paper, which turned violet in ozone, yellow in nitrogen dioxide, and was not affected by hydrogen peroxide. Ozone darkens (oxidizes) a clean silver plate which has just been held in a flame to get a trace of oxide (catalyst).

Exercise 9. — Compare the properties of oxygen and ozone.

Exercise 10. — Describe four methods of making oxygen.

Exercise 11. — What are oxides? Name some that are solids; liquids; gases.

Exercise 12. — Give two examples of an exothermic reaction.

Exercise 13. — What is catalysis? Examples?

Exercise 14. — Of what importance is it to fish that oxygen is slightly soluble in water?

Exercise 15. — How could you remove dissolved air from water?

Exercise 16. — How did Lavoisier prove that oxygen is one fifth of air by volume?

Exercise 17. — Burn 100 g. of magnesium (flash light metal). Does the ash weigh more or less than 100 g.? How about a candle?

Exercise 18. — Why select oxygen as the first element to study?

Review Suggestions

You have now studied two chapters. It is time to form the invaluable habit of *constantly reviewing.* Out of every two hours you use in preparation for a lecture spend one fourth of the time, half an hour, in review and make it the *first half hour.* Otherwise you will find the time gone on the advanced lesson with no review. Your intentions to catch up some day will be excellent, but such intentions are too often not made good.

Write equations constantly. Repeat those in the text and think up others to describe every reaction you have observed.

Do not read your lesson three times and assume that because you clearly understood every statement as you read it you have a thorough grasp of the chapter. The test of your knowing the lesson is this: Can you shut the book and write an outline of the leading topics and then tell to yourself the leading facts under each topic head? Be as critical of your knowledge as your teacher may be on quiz day. Most students coddle themselves.

Skim the chapter to get a birdseye picture of it. Then carefully read the first topic once, shut the book and tell yourself the main points of that topic. See if you are right. Read the next topic the same way. On finishing the last topic you will know the lesson.

Do not commit to memory the atomic weights. You will learn formulas by using them. Remember only the most important properties of substances.

CHAPTER III

THE PROPERTIES OF GASES AND THE THREE STATES OF MATTER

Gases expand indefinitely to fill any spaces in which they are inclosed. In addition they have great compressibility. By the application of great pressure oxygen can be reduced to one two-hundredth of its volume under ordinary pressures. Solids and liquids, on the other hand, have comparatively little compressibility.

Boyle's Law. — Boyle (1660) observed that *the volume occupied by the same sample of any gas varies inversely with the pressure.* Accurate measurements showed him that if he doubled the pressure on a liter of a gas (keeping the temperature constant) the volume became only half a liter. With three times the pressure the volume became one third of a liter. This generalization can be formulated mathematically thus:

$$\frac{P_1}{P_2}=\frac{V_2}{V_1} \text{ or } P_1V_1=P_2V_2 \text{ or } V_1=V_2+\frac{P_2}{P_1},$$

where P_1 and V_1 are the first pressure and volume and P_2 and V_2 any other pressure with its accompanying volume. Since the product P_1V_1 is equal to any other pressure-volume product for the same weight of the gas, it is sometimes said that the product of the pressure times the volume of a gas is a constant. Boyle's law can even be plotted as a curve. In Fig. 12 OV is the abscissa and OP the ordinate. We may measure any given pressure along OP in its proper number of units, say P_1. The corresponding volume of the gas may be measured along OV as the distance V_1. Other volumes and pressures of the same sample of gas may be plotted as P_2, V_2, etc. From the point P_1 a dotted line is extended at right angles

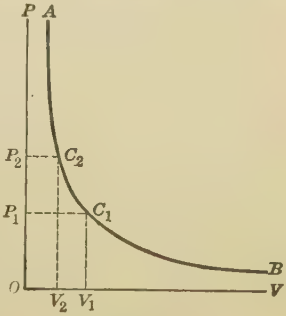


FIG. 12

to OP and from V_1 a similar line at right angles to OV. These intersect at C_1. Other intersections at C_2, etc., may be marked. When several such intersections are marked a smooth curve is drawn through them, such as AB. This curve is a graphic representation of the law and is termed a rectangular hyperbola.

It is our custom to refer to the average atmospheric pressure at sea level (enough to hold up a 760 mm. column of mercury in a barometer) as the standard pressure.

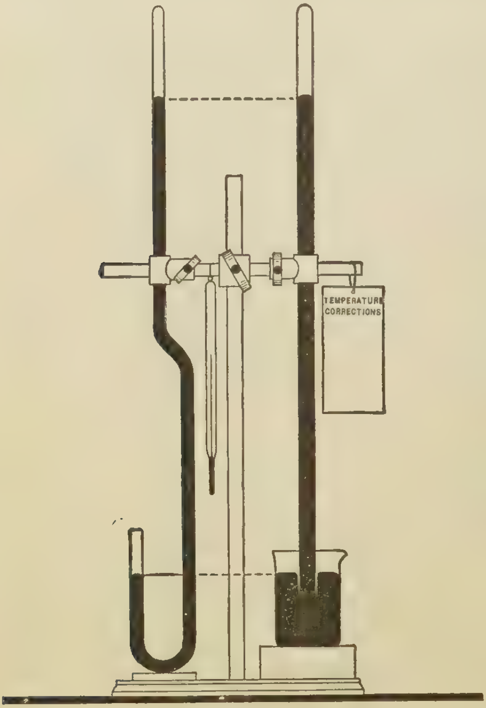


Fig. 13

The simplest form of a barometer (on the right in Fig. 13) consists of a tube, over 760 mm. long, filled with mercury and inverted in a cup of mercury. The pressure of the air holds up the mercury in the tube to a height of about 760 mm. at sea level. If the tube is longer there is a vacuum at the top. The cup may be dispensed with by using the form of tube represented on the left.

A man buying a million liters of a rare and expensive gas could be cheated if he failed to stipulate the pressure. Since gases expand indefinitely, even a very little mass of a gas could occupy a million liters volume. We do not always measure gases at exactly 760 mm. pressure, but we calculate from Boyle's law what the volume would be if the pressure were changed to the standard 760 mm. For example, 400 cc. of air at 740 mm. would occupy what volume at 760 mm.? Using the formula

$$V_1 = V_2 \times \frac{P_2}{P_1},$$

we may let V_1 represent the volume to be calculated and P_1 the standard pressure, 760 mm. To make it clearer

$$V\ (\text{standard}) = V\ (\text{observed}) \times \frac{P\ (\text{observed})}{P\ (\text{standard})}$$

Substituting, we have

$$V\ (\text{standard}) = 400 \times \tfrac{740}{760} = 389 \text{ cc.}$$

To aid the memory one merely recalls that the observed volume is multiplied by a fraction with the two pressures for its terms. Also if the change to 760 mm. means *greater* pressure, the gas will contract and therefore the numerator must be the smaller value. The calculation is similar if the change to 760 mm. means *less* pressure and consequent expansion.

Exercise 1. — Convert 420 cc. of dry gas at 740 mm. to the volume at 760 mm.

Exercise 2. — Convert 800 cc. of dry gas at 768 mm. to the volume at 760 mm.

Charles' Law (Gay-Lussac's) and the Absolute Temperature.—Charles in 1787 observed that on cooling any gas from 0° C. to −1° C. it contracted 1/273 of its volume. It was a simple inference that if cooled 273° C. its volume would be nothing at all. However, in practice all gases become liquid before they have been cooled 273° C. below 0° C., and after it becomes liquid a substance no longer obeys Boyle's law of gases. The most difficult gas to liquefy was helium, which had to be cooled to −268.7° C. There is a real convenience, however, in calling this imaginary point of no volume ***absolute zero***, −273° C.

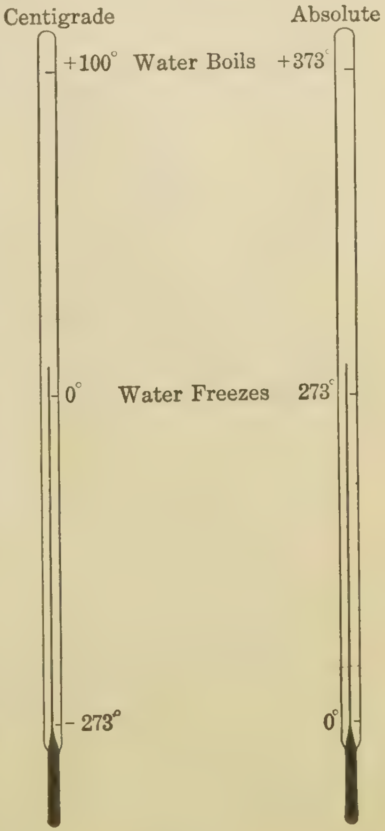


Fig. 14

Figure 14 shows the relations between the two temperature scales. To change from a Centigrade reading we merely add 273° to get the absolute temperature. For example, 17° C.=17°+273° =290° Absolute.

Exercise 3. — Convert −25° C. into the absolute temperature.

Charles' law is merely an observation that *the volume of a given sample of a gas varies directly as the absolute temperature* (if the pressure is kept constant). For example, to double the volume that a gas occupies at 20° C. by heating we should need to heat not to 40° C. but to double the absolute temperature. 20°+273°=293° Absolute; so double this temperature would be 586° Absolute or 313° C.

When heated to 313° C. the gas would have twice its original volume. Charles' law is, therefore, formulated as follows:

$$\frac{V_1}{V_2}=\frac{T_1}{T_2} \text{ or } V_1=V_2\times\frac{T_1}{T_2},$$

where T_1 and T_2 refer to absolute temperatures. When we speak of a liter of oxygen weighing 1.429 g. we mean a liter at 760 mm. pressure and 0° C. Since gases expand on heating, there can be no accuracy without reference to a definite *standard temperature.* Obviously we do not care to measure gases in rooms at 0° C., but we can apply Charles' law and calculate what the volume would be if the gas were cooled to 0° C. For example, 400 cc. of air measured at −18° C. has what volume at 0° C.?

$$V \text{ (standard)} = V \text{ (observed)} \times \frac{273}{273 \pm t^\circ}$$

where $t°$ is the Centigrade temperature. Substituting values,

$$V \text{ (standard)} = 400 \times \frac{273}{255} = 428 \text{ cc.}$$

When confused one can recall that the observed volume is multiplied by a fraction with absolute temperatures for its terms and that if the change is to a *higher* temperature the gas will expand, occupying more volume; therefore the numerator must be larger than the denominator. The observed volume of a gas can be brought to 760 mm. and 0° C. by applying both connections at once. For example, 400 cc. of air at 740 mm. and −18° C. would have what volume standard?

$$V \text{ (standard)} = V \text{ (observed)} \times \frac{740}{760} \times \frac{273}{255} = 417 \text{ cc.}$$

760 400

EXERCISE 4. — Convert 180 cc. of dry gas at 14° and 775 mm. to its volume at 0° and 760 mm.

Law of Partial Pressures. — Dalton noted that the total pressure of a mixture of gases was the sum of the pressures that would be exerted by each gas if the others were not present (temperature being the same). All gases collected or measured over water have water vapor present, which exerts a part of the total pressure. To learn the actual pressure exerted by the dry gas we must subtract the pressure due to water vapor at the given temperature. To show how the values for the pressure of water vapor can be obtained we can fill a tube over 760 mm. long with mercury and, closing the end with a thumb, invert the tube, placing the open end in a dish of mercury. The mercury is held up to some definite height, depending on the pressure of the air, 760 mm. at sea level. We have thus a simple form of the *barometer* for measuring air pressures. If, now, we force a few drops of water (by a medicine dropper) under the tube, the water rises into the vacuum at the top, turns to vapor, and exerts pressure downward on the column of mercury. The mercury falls several millimeters, depending only on the temperature. To determine the pressures at different temperatures the tube can be surrounded with a jacket through which flows water at desired temperatures. A table of "aqueous tension" values is given in the Appendix. Since we measure most gases over water, the gases are saturated with moisture at the given temperatures. Suppose the problem is to correct to standard conditions 400 cc. of air collected over water at 740 mm. and 18° C. Now the *observed pressure* of 740 mm. is not all due to the air, but 15.46 mm. of it is due to water vapor. Therefore

$$V_1 \text{ (standard)} = V_2 \text{ (observed)} \times \frac{740 - 15.5}{760} \times \frac{273}{291} = ? \text{ cc.}$$

NOTE: A table of corrections for the expansion of the mercury column due to heating above 0° C. is found attached to the barometer.

EXERCISE 5. — Convert 200 cc. of air measured over water at 23° and 780 mm. to the volume under standard conditions.

Graham's Law of Diffusion. — All gases mix homogeneously unless they react. Bromine is a heavy gas, but if a little is released at the bottom of a tall cylinder of air the bromine can soon be smelled at the top, rising against the force of gravitation. Finally the air and bromine will be uniformly mixed. Hydrogen is the lightest gas, and yet if some of it is released at the top of a tall closed cylinder of air the hydrogen will diffuse to the bottom and a uniform mixture result.

W. H. Chapin's apparatus (Fig. 15) for demonstrating Graham's law is very useful. *A* is a cylinder about 16 in. high, *B* is a porous clay cup connected with *A* by a funnel and rubber band or by a rubber stopper, and *C* contains water saturated with the gas used. After the apparatus has been filled with the gas desired the pinch clamp *E* is closed, *D* opened and the exact time taken while the water rises from *N* to *M*. Of course the gas diffuses through the thousands of minute holes in the porous cup. The experiment may be repeated with other gases and their rates of diffusion compared.

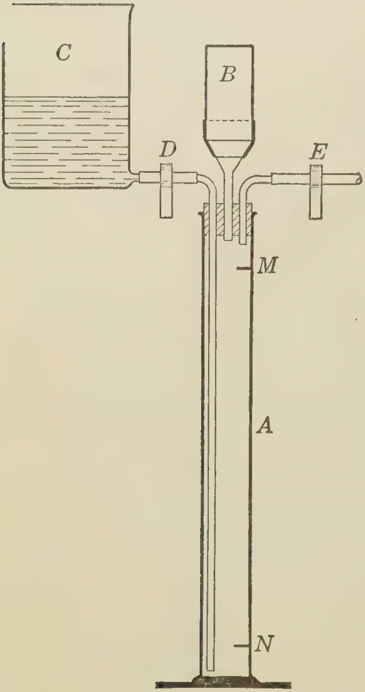


FIG. 15

Graham measured the rates at which gases diffuse through minute holes and found that *the speed of diffusion of gases varies inversely as the square roots of their densities.* Oxygen is about sixteen times as heavy as hydrogen, hence hydrogen diffuses four times as fast as oxygen. Let R_1 represent the rate of diffusion for oxygen and R_2 the rate for hydrogen; D_1 the density of oxygen and D_2 the density of hydrogen:

$$\frac{R_1}{R_2} = \frac{\sqrt{D_2}}{\sqrt{D_1}} = \frac{\sqrt{1}}{\sqrt{16}} = \frac{1}{4}.$$

EXERCISE 6. — A liter of carbon dioxide weighs 1.9768 g. and a liter of nitrogen weighs 1.2507 g. Compare their rates of diffusion accurately.

The Kinetic Theory of Gases. — To explain the facts expressed in the laws of Boyle, Charles and Dalton, as well as certain other facts, it is believed that the molecules of a gas are relatively very far apart, moving rapidly in straight lines until they collide with other molecules, yet rebounding with such perfect elasticity that there is no loss of motion. Cohesion has but little effect on the molecules of a gas. Pressure is due to the impacts of molecules. The velocity of molecular motion is increased by rise in temperature.

Since all gases react alike to change in pressure and temperature, they must all have the same structure. The enormous compressibility of gases is strong evidence in favor of the kinetic theory. On this assumption compression merely means a decrease in the spaces between molecules — bringing molecules closer together. Reliable experimental evidence has recently shown that at 0° C. and 760 mm. 1 cc. of any gas contains 2.7×10^{19} molecules and yet the average distance between molecules is about thirteen times their average diameter.

Imagine a one-liter cylinder closed with a smoothly moving plunger. If the pressure exerted by the plunger is doubled by adding weights, the plunger sinks to the halfway mark and the volume of the gas becomes one half a liter. Now the plunger is upheld by the opposing pressure of the gas which has just been doubled. Why? Obviously the same number of molecules is contained in one half the space after the extra compression. This means that twice as many molecules strike the plunger per second as before, thus *accounting for the fact of doubled pressure.*

Figure 16 makes this clear with a convenient but ridiculously erroneous number of molecules represented. As was stated before a very small mass of any gas expands indefinitely, filling any vessel no matter how large. Pressure is exerted on the cover of such a vessel. This could not be true if gases exerted pressure like the thrust of a spring or the downward and sidewise thrust of a liquid. Gas pressure is exerted in all directions and has no limit in distance. The spring has its limit. The theory that gas pressure is produced by the impacts of separate moving particles is in accord with the facts of gas pressure. The walls of containing vessels are pounded with a hailstorm of particles moving at 0° C. at a speed of one quarter of a mile per second.

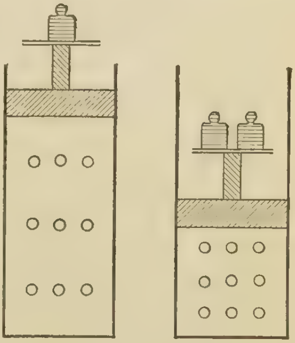


FIG. 16

Heat is merely the evidence of molecular motion. *Absolute zero* now takes on a new meaning. It is the temperature of no molecular motion. A rise in temperature increases pressure by increasing the kinetic energy of the flying molecules, which equals $1/2\ ms^2$ (where m is the mass and s the speed of the molecule). But such experiments as weighing a closed vessel full of gas at different temperatures show no change in m, therefore it is only the speed that changes with temperature.

A corollary to this, reminding us of Graham's law of diffusion, is found in the fact that doubling the absolute temperature of a gas, heavy or light, doubles the pressure (if the volume be kept constant). Now the pressure varies with $1/2\ ms^2$ in each case but if we compare oxygen molecules with hydrogen molecules with masses as 16: 1 we see that doubling the speed in each case would increase $1/2\ ms^2$ far more for oxygen than for hydrogen. Yet the laboratory facts show that with *equal rise in temperature the pressure increase is the same for all gases!* Evidently the change in speed adjusts itself accordingly, so we are ready to believe that the speed increase due to temperature rise is inversely proportional to the square root of the density of a gas. Heavy molecules are not moving as fast as lighter ones at a given temperature.

The open structure of gases explains their ease of diffusion and perfect mixing. It also explains the law of Partial Pressures. No wonder each gas in a mixture can bombard the walls of containing vessels just as readily as if other gases were not present. There is enough of free space between molecules to permit other particles to move freely.

Cohesion between molecules of a gas counts for very little because they are so far apart and, at elevated temperatures, moving with such great velocity. But on cooling, their kinetic energy decreases and the molecules come close enough to each other to allow their mutual attraction (cohesion) to become a powerful factor. The gas may then become a liquid. At very high pressures, then, gases decrease in volume more than could be predicted by Boyle's law, due to this helping effect of cohesion. There is another factor which introduces a deviation from the gas laws. At ordinary pressures a liter of gas is mainly space, but when highly compressed the part of the total volume occupied by actual molecules becomes noticeable. Since Boyle's law holds only for the change in free space, it loses in accuracy at high pressures. The extent of deviation is shown for several gases in the following table.

The volumes indicated are those occupied at 0° by two liters of each gas when the pressure is increased from one atmosphere to two atmospheres. They should all be exactly one liter if Boyle's law held perfectly.

Hydrogen	1.0006 liters
Nitrogen	0.9996 liter
Oxygen	0.9991 liter
Carbon dioxide	0.9931 liter
Ammonia	0.9845 liter
Sulfur dioxide	0.9739 liter

The gases that are liquefied most easily, such as ammonia and sulfur dioxide, depart furthest from this law. At high pressures a point is reached where all gases that do not liquefy are compressed less than they should be in accordance with this law. The greater compressibility under moderate pressures is caused by the attraction of molecules for each other — the same forces which cause the gas to liquefy at low temperatures or under pressure. The point of too little compressibility is reached when the molecules are brought so close together that the molecules themselves fill a considerable fraction of the total space.

In liquids and solids cohesion is a tremendous factor because the molecules are in frequent contact. Yet the molecules are moving even here, although in shorter free paths. Evaporation of liquids, their vapor pressure, and the fact that increase of temperature transforms solids and liquids into gases, all confirm this view. Mercury is easily volatilized, but we are thankful that tungsten is not, for otherwise tungsten electric lamps would not last long. Sugar, as we have learned already, decomposes without volatilizing.

Avogadro's Law. — All the preceding facts, and some others to be considered later, led Avogadro in 1811 to the theory that *equal volumes of all gases at the same temperature and pressure contain equal numbers of molecules.* Until 1860 science paid little attention to this speculation, but we are now convinced of its truth.

Exercise 7. — A given quantity of gas has a volume of 15 liters at 740 mm. On coördinate paper plot a curve (as in Fig. 12), showing the application of Boyle's law when the pressure is changed to 150 mm., 200 mm., 250 mm., 300 mm., and 500 mm.

Exercise 8. — A liter of oxygen at 760 mm. is forced into a vessel containing a liter of nitrogen at 760 mm. What will be the resulting pressure?

The student must remember that a scientific "law" is merely a statement of facts observed in the laboratory and is no more accurate than those observations. Laws are convenient expressions of facts.

The Three States of Matter

Solids retain their shape, liquids take the shape of the containing vessel, while gases expand indefinitely. There is great freedom of molecular movement in gases and comparatively little in solids and liquids. Whether a substance is in the solid, liquid or gaseous state at a given temperature and pressure depends on the relative influence of the forces of cohesion and the kinetic energy of the molecules.

Transformations.— Kinetic energy must be consumed in order to bring about the change:

$$\text{Solid} \rightarrow \text{liquid} \rightarrow \text{gas}.$$

The forces of cohesion must be overcome in order to allow the increased freedom of molecular motion called for by the change of state.

Melting Point and Heat of Fusion. — To increase the freedom of movement of the molecules of a solid so that a fluid results requires increased kinetic energy. This is given by heating the solid. Heat breaks up the crystalline arrangement of a solid. There is a rise in temperature until some liquid is formed and then no further rise until all the solid is melted. The temperature at which this occurs is called the *melting point*. Any additional kinetic energy given the liquid is used in tearing off molecules of the solid. To convert one gram of ice at 0° into liquid water, 79 cal. of heat are required. This is termed the ***heat of fusion*** of ice. The corresponding value for sulfur is 9.37 cal. and for aluminum 76.8 cal.

If a solid contracts on melting, any increase of pressure must lower the melting point. Thus ice at 0° is converted into water by considerable increase in pressure. On release of this pressure the water changes back to the solid form.

Boiling Point. — When the kinetic energy of a liquid is increased (by heat) so that its vapor pressure just equals the pressure of the atmosphere above it, the liquid boils. The *boiling* *point* is the temperature at which this occurs. Obviously it varies with the pressure of the atmosphere. Water boils at 100° under an atmospheric pressure of 760 mm., but at one half an atmosphere it boils at 82° and at two atmospheres the boiling point is 121°. Boiling points recorded in the text all refer to the standard atmospheric pressure, 760 mm. The ebullition observed in any boiling liquid is due to the expansion of bubbles of vapor forming within the liquid.

Heat of Vaporization. — On heating a liquid its temperature rises to the boiling point and then remains constant (if the pressure is constant). The additional heat is consumed in forcing the change of state from liquid to gas, since this change consumes energy. By the ***heat of vaporization*** of a liquid we mean the number of calories required to convert one gram at the boiling point into vapor. In the case of water this is 540 calories.

Critical Temperature. — On compression gaseous molecules can be brought so close together that their own attractive forces restrict their motion greatly and liquefaction results. The lower the temperature the less the pressure required to overcome the kinetic energy of the molecules. Yet for every gas there is a temperature above which no pressure, however great, can overcome this kinetic energy and produce liquefaction. This is called the ***critical temperature.*** The pressure required to liquefy a gas at its critical temperature is its "critical pressure." The subject will be discussed further under the topic "Liquefaction of Gases."

CHAPTER IV

HYDROGEN

History. — The discovery of hydrogen should be credited to Turquet de Mayerne (1650), who treated iron with dilute sulfuric acid and recognized the "inflammable air" formed as a distinct substance. Paracelsus had really done the same thing a century earlier but failed to recognize it as a distinct substance. Cavendish in 1766 discovered many of its properties. Lavoisier named it "Hydrogen," meaning "water former," although it was Cavendish who burned hydrogen in oxygen and proved that water was composed of hydrogen and oxygen only.

Occurrence. — Hydrogen does not occur free in nature except for traces in the air and in some rocks and a considerable amount in gases erupted by very violent volcanic outbursts. All this is negligible. But in the combined form it is found in water, plant and animal tissues, petroleum, asphalt and natural gas. Among laboratory reagents we learn that it is an essential element of all acids and bases.

Preparation. — 1. *Metals and Acids.* Since hydrogen is a constituent of such common materials as water, acids, and bases, these must be the sources for its convenient preparation. In the laboratory it is extremely convenient to displace hydrogen from dilute acids by the more active metals. The hydrogen is collected by displacement of water, as in Fig. 17:

$$\begin{aligned} Zn + 2\,HCl &\rightarrow ZnCl_2 + H_2 \\ Zn + H_2SO_4 &\rightarrow ZnSO_4 + H_2 \\ Fe + H_2SO_4 &\rightarrow FeSO_4 + H_2 \\ 2\,Al + 6\,HCl &\rightarrow 2\,AlCl_3 + 3\,H_2 \end{aligned}$$

The less active metals such as copper, mercury, platinum, gold and silver do not displace hydrogen from acids. Some acids react more readily than others for reasons to be developed later. Pulverized metals naturally react more rapidly than do masses of metal because the greater surface allows better contact. A strip of very pure zinc is not attacked by dilute sulfuric, but if a less active metal such as copper be dropped in the acid and placed in contact with the zinc, hydrogen is released rapidly on the surface of the copper, although it is the zinc that is really attacked. The two metals form an electric "couple." Impurities in commercial zinc form many small local couples which make it react readily with acid.

2. *Metals and Bases.* — Several active metals displace hydrogen from bases. In some cases a strong solution of the base is used; in others the powdered dry metal and base are heated together:

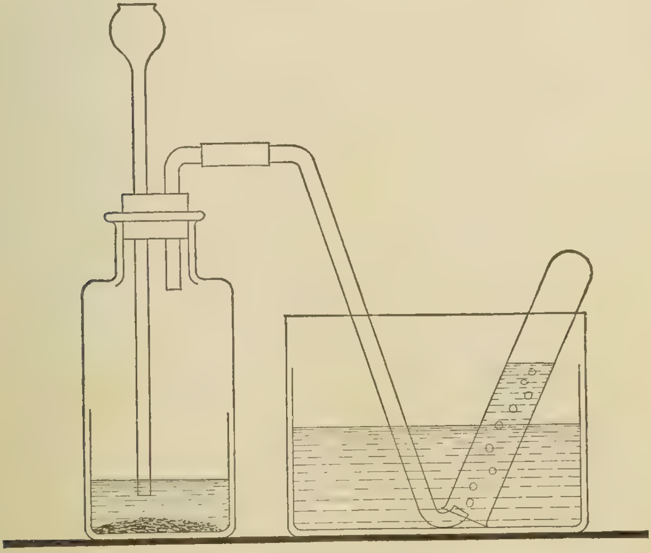


FIG. 17

$$Zn + 2\ NaOH \rightarrow Zn(ONa)_2 + H_2$$
$$2\ Al + 6\ NaOH \rightarrow 2\ Al(ONa)_3 + 3\ H_2$$

The first product is called sodium zincate and the second sodium aluminate.

3. *Metals and Water.* — The most active metals, such as potassium and sodium, displace hydrogen from cold water violently. In fact a bit of such a metal the size of a pea is adequate

for the experiment and it is well to take due precautions. The hydrogen is often ignited from the heat of reaction:

$$2\ K + 2\ H_2O \rightarrow 2\ KOH + H_2$$
$$2\ Na + 2\ H_2O \rightarrow 2\ NaOH + H_2$$
$$Ca + 2\ H_2O \rightarrow Ca(OH)_2 + H_2$$

An alloy of 65% lead and 35% sodium called "Hydrone" reacts rapidly but safely with water. The lead merely dilutes the sodium. An alloy of mercury and sodium (an amalgam) is also a safe hydrogen former for similar reasons. Calcium acts at moderate speed (Fig. 18). In all cases the products are hydroxides of the metals used, sodium hydroxide, $NaOH$, for example. It is to be noted that only half the hydrogen in the water is displaced, no matter how much metal is used.

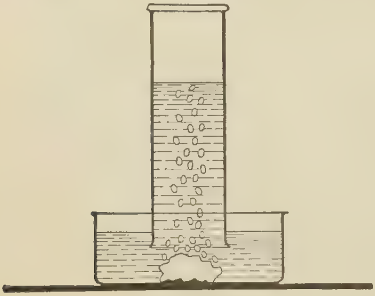


FIG. 18

EXERCISE 1. — From the topic "Metals and Bases" could you learn how to displace the remaining half of the hydrogen in water?

EXERCISE 2. — Lithium, although not a common metal, is nearly as active as sodium. Represent by an equation its reaction with water.

Less active metals react with water only when heated. Magnesium displaces hydrogen from boiling water if a little of a magnesium salt is present to keep the surface of the metal clean. Steam passed over red-hot iron reacts as follows:

$$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4\ H_2.$$

This is one of the great commercial methods of obtaining hydrogen. At such high temperatures as are used the oxides form because any possible hydroxides would be decomposed into oxides and water.

4. *Electrolysis.* — When a current of electricity is passed through water, made conducting by the presence of some substance such as sulfuric acid or sodium hydroxide, we are able to collect two volumes of hydrogen at the cathode to one of oxygen at the anode (Fig. 19). Since this is the exact proportion in which they unite to form water on burning, the experiment adds convincing

proof to our ideas on the composition of water. A detailed explanation of the action of the dissolved acid or base will be given under "Ionization." Yet it may be stated now that a small amount of sulfuric acid, for example, enables us to decompose an unlimited amount of water. Is the water a catalyst in this case?

5. ***Commercial Methods.*** — The industrial use of hydrogen has increased by leaps and bounds in the past few years. In 1914 over 250,000 tons of liquid fats were "hardened" by the catalytic addition of hydrogen in Europe alone. Since that time the development of the Haber process for making ammonia from nitrogen and hydrogen has vastly increased this demand. The influence of the Great War in advancing the airship and balloon industry has created a need for hydrogen in very great quantities.

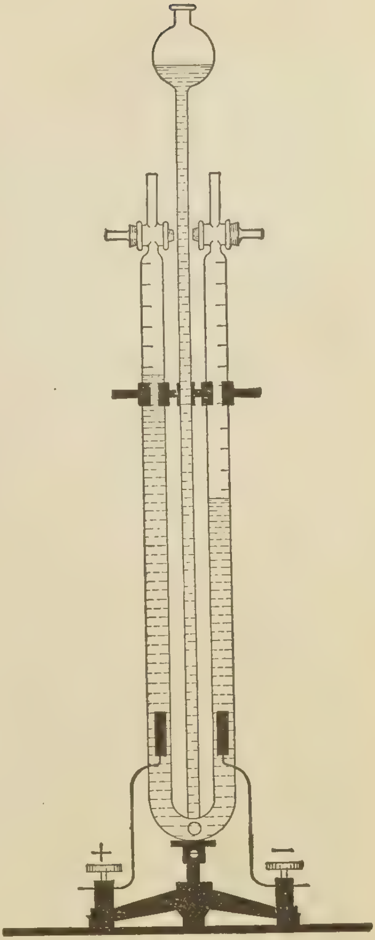


FIG. 19

This growth in the industry has almost revolutionized the older methods of manufacture. It brought into prominence the "Silicol" process:

$$Si + 2\ NaOH + H_2O \rightarrow Na_2SiO_3 + 2\ H_2.$$

The element silicon (or in practice ferro-silicon containing 82–92% Si) is slowly added to a 25% solution of sodium hydroxide in water. The reaction begins at a satisfactory rate when the temperature reaches 90° C. and this can be secured by the heat of solution of the sodium hydroxide. The great advantage of this process for military purposes lay in the very great production per hour from a portable plant of small cost. However, the raw materials are still too expensive except for war emergencies.

The Linde-Frank-Caro Process makes use of the fact that a very low temperature greatly aids in the liquefaction of a gas by high pressure. "Water gas" is first made by passing steam over coke at 1000° C.:

$$C+H_2O \rightarrow CO+H_2.$$

This mixture of carbon monoxide and hydrogen is cooled to about −200° C. by allowing certain liquefied gases to evaporate around the container, and a pressure of twenty atmospheres is then applied. The carbon monoxide and some impurities liquefy, while the hydrogen is removed as a gas, since it cannot be liquefied above −234° C., its critical temperature.

Another method promising great efficiency is the Badische Catalytic Process. Water gas (H_2+CO) and steam are passed over a catalytic mixture of the oxides of iron, nickel and chromium:

$$H_2+CO+H_2O \rightarrow 2\ H_2+CO_2.$$

The steam oxidizes the carbon monoxide. The mixed gases are bubbled under pressure through water, which takes out the carbon dioxide. This a continuous process and very economical.

The Iron Contact Process, however, furnishes most of the world's hydrogen to-day, although its supremacy is threatened. Steam is passed over red-hot iron:

$$3\ Fe+4\ H_2O \rightarrow Fe_3O_4+4\ H_2.$$

As soon as the reaction ceases, because of the formation of a protecting film of oxide, water gas is turned on for twenty minutes:

$$Fe_3O_4+4\ H_2 \rightarrow 3\ Fe+4\ H_2O,$$
$$Fe_3O_4+4\ CO \rightarrow 3\ Fe+4\ CO_2.$$

The water gas is then shut off, more steam turned on for ten minutes, and more hydrogen thus produced. By alternate use of steam and water gas the same mass of iron is used indefinitely. The electrolytic process is used to some extent commercially. It produces a very pure hydrogen. If a solution of sulfuric acid is used the electrodes should be of lead: if a solution of sodium hydroxide is used iron electrodes can be used without attack by the liquid. The demand for oxygen, a by-product in this case, helps to reduce the cost of hydrogen.

A considerable amount of hydrogen has been secured as a by-product in the electrolysis of salt water. Here sodium chloride (NaCl) is decomposed to form chlorine gas (useful in bleaching and sterilizing) and sodium, which reacts with the water present to yield sodium hydroxide and hydrogen.

Purification of Hydrogen. Nascent State. — The zinc, iron or other metals used in the preparation of hydrogen usually contain impurities that form offensive hydrogen compounds. To purify the gas it is first bubbled through water to catch any spray of droplets of generating solution. All gases coming out of a liquid carry a spray just as do winds from the ocean waves. A loose wad of cotton is often used to hold the droplets. Next the gas is passed through a dilute alkaline solution of potassium permanganate, a compound which readily gives up its oxygen to substances capable of taking it on. In other words potassium permanganate oxidizes the impurities into compounds retained by the solution while the hydrogen passes on unchanged and may be dried by a tube of anhydrous calcium chloride.

If the hydrogen is generated in direct contact with the oxidizing agent, for example by putting zinc, acid, and permanganate all in the same tube, much of the hydrogen unites with the oxygen of the permanganate to form water. The solution is decolorized, yet if pure hydrogen from another vessel be passed through a solution of permanganate, there is no loss of color. Two theories are offered. One that hydrogen in its ordinary molecular form (H_2) is not very active at ordinary temperatures but at the instant of release from compounds the single atoms of hydrogen have great activity, some combining in twos to form the gas molecules, and others reacting with substances in immediate contact. This transient atomic condition is called the *nascent state*.

The other and more modern theory is that the increased activity of the hydrogen at the instant of release from compounds is due to the catalytic effect of the metal surface, zinc in the example cited. Since different metals have different influences on the rate of this attack on the permanganate, we are inclined to favor the latter theory.

Physical Properties. — Hydrogen is a colorless, odorless, tasteless gas. A liter weighs 0.08987 g. at standard conditions, so it is the lightest substance known. It may be poured upward (Fig. 20)

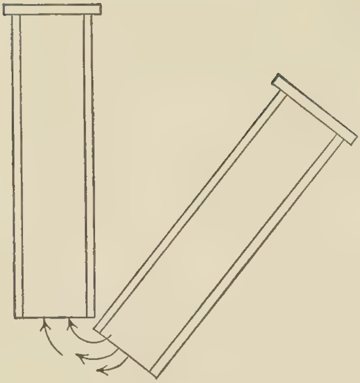


Fig. 20

from cylinder to cylinder. At ordinary temperatures and 760 mm. pressure 2 cc. will dissolve in 100 cc. of water. It cannot be liquefied above −234° C., its critical temperature. It has been frozen at −259° C. into a transparent, ice-like solid. It is absorbed by metals to a marked extent. Powdered palladium under favorable conditions has absorbed 900 times its own volume of hydrogen. This property of dissolving in metals probably explains in part why hydrogen passes through thin sheets of hot gold, platinum and other metals. Of course, as indicated under Graham's law, it has the greatest speed of diffusion of all gases and this is another factor. The loss by diffusion through balloon fabric is a serious problem.

Exercise 3. — A balloon is inflated near the ground. At a great height it expands, since the air pressure around it is less. Will the leakage by diffusion change?

When a large beaker of hydrogen is placed over a porous cup, connected as in Fig. 21, bubbles of air rise through the water in the bottle. Hydrogen diffuses into the cup faster than air diffuses out, hence pressure is developed.

Chemical Properties. — Hydrogen is rather inactive at ordinary temperatures, but at higher temperatures unites with most of the nonmetals and many of the metals:

$$S + H_2 \rightarrow H_2S,$$
$$Cl_2 + H_2 \rightarrow 2\ HCl,$$
$$O_2 + H_2 \rightarrow 2\ H_2O,$$
$$N_2 + 3\ H_2 \rightarrow 2\ NH_3.$$

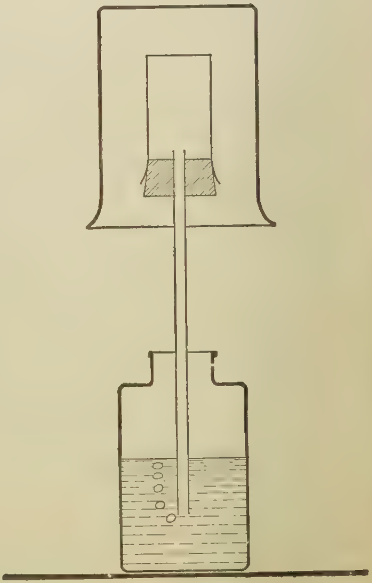


Fig. 21

Hydrogen unites with hot sulfur vapors at 250° to form the offensive gas, hydrogen sulfide. With chlorine gas it reacts when hot to form hydrogen chloride (which in water solution is hydrochloric acid). A jet of hydrogen, or even illuminating gas, burns in a jar of chlorine just as truly as it burns in a jar of oxygen. A mixture of chlorine and hydrogen can be exploded by a bright light. The Haber process of uniting hydrogen with nitrogen has already been mentioned as of tremendous importance in the recent war. It is by no means as simple as the equation indicates, but it is very efficient. Nitrogen and hydrogen react to form ammonia when electric sparks are passed through their mixture.

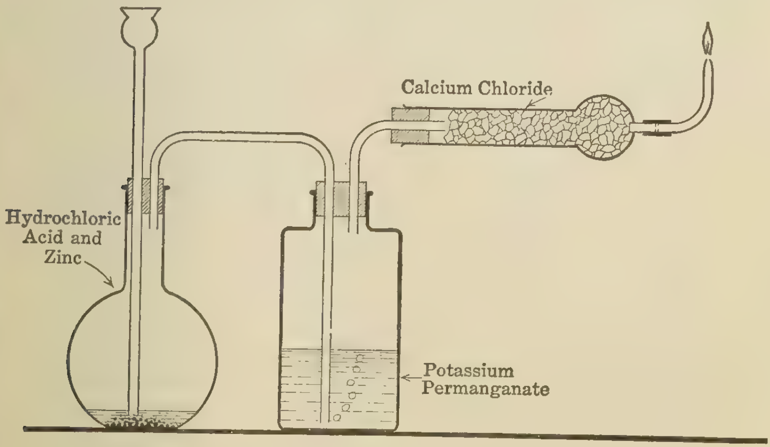


Fig. 22

The hydrogen flame is intensely hot, as 34,215 calories are released when one gram of hydrogen burns. That water is formed can be shown by holding a cold, dry beaker above the flame. Drops of moisture condense on the glass. The hydrogen may be purified by contact with a solution of potassium permanganate and dried over anhydrous calcium chloride (Fig. 22). A great deal of heat is wasted when hydrogen burns in air. Not only does the nitrogen interfere with good contact between the reacting elements but it cools the flame by absorbing heat. That is why a flame can be "blown out" by the cooling effect of too much air. A special burner, called the oxyhydrogen blowpipe (Fig. 23), has been devised for the proper mixing at the nozzle of a stream of oxygen and a stream of hydrogen. In this flame platinum melts and silver boils. The temperature ranges from 1800° C. to 2500° C., as conditions vary. Hydrogen burns with a colorless flame unless a glass tip or something of the sort is used. Then the sodium compounds in the glass color the flame yellow.

The reaction between oxygen and hydrogen is neglible at room temperature; a noticeable amount reacts in a few hours at 518° C.; at 600° C. the reaction is rapid, and at 700° explosive. This means it requires a flame or red-hot solid to ignite the mixture. Platinum, finely divided, catalytically speeds up the trifling reaction at ordinary temperatures to a point where it becomes incandescent with the heat evolved. It then ignites the mixture. Gas lighters make use of this principle.

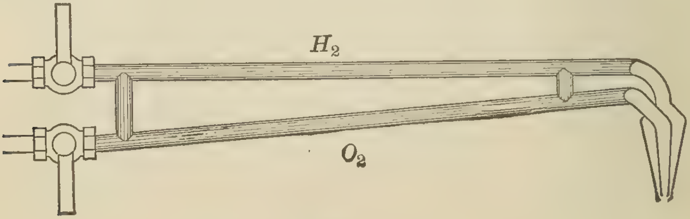


FIG. 23

Morley of Western Reserve University spent years of marvelously accurate work in ascertaining the exact weights of hydrogen and oxygen combining to form water. His results, the most accurate known, indicate that 1 part by weight of hydrogen unites with 7.94 parts of oxygen. Morley also measured with great accuracy the proportion by volume in which oxygen and hydrogen unite to form water. This proportion is 2.0027 volumes of hydrogen to 1 volume of oxygen. Long before Morley's time it was known that two volumes of hydrogen unite with one volume of oxygen to form two volumes of water (as vapor). Morley redetermined these ratios with greater accuracy than that of previous measurements.

This interesting ratio, and many others, led Gay-Lussac to state that *whenever in any chemical reaction gases appear or disappear they do so in the ratios of small whole numbers by volume.* A mixture of any two gases in the proportion called for by Gay-Lussac's Law is violently explosive. Any excess of either gas dilutes the mixture and reduces the explosiveness. In fact, a considerable excess of either gas may prevent explosion.

Hydrogen, when hot, removes oxygen and even some other elements from many compounds, a process called ***reduction***, the exact opposite of *oxidation*. Fig. 3 represents the reduction of heated copper oxide by dried hydrogen. The water formed is taken up by the calcium chloride in the U tube:

$$CuO + H_2 \rightarrow Cu + H_2O.$$

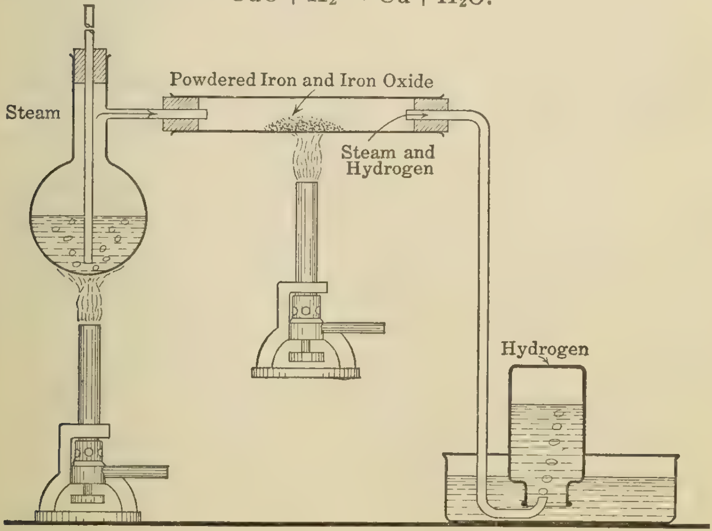


FIG. 24

Reversible Reactions. — The mysterious attraction that holds elements together is sometimes called ***chemical affinity***. When hot hydrogen ***reduces*** some metallic oxide, that is, steals oxygen away, we are tempted to say that this occurs because hydrogen has a greater affinity for oxygen than has the metal. Consider iron oxide, for example:

(1) $$Fe_3O_4 + 4\ H_2 \rightarrow 3\ Fe + 4\ H_2O.$$

A stream of hydrogen passed over the hot oxide reduces it to the metal by stealing the oxygen. Apparently iron does not have the force to hold its own. If through the same tube we pass a current of steam (Fig. 24), the following reaction occurs:

(2) $$3\ Fe + 4\ H_2O \rightarrow Fe_3O_4 + 4H_2.$$

The steam oxidizes the iron back to the oxide, leading us to the conclusion that iron removes the oxygen from steam because it has a greater affinity for oxygen than has hydrogen. But here are two conflicting conclusions. Both cannot be true. Now if we seal iron and water in a strong closed tube and heat it for a time, we find on opening the tube all four substances,—iron, hydrogen, steam and iron oxide. Evidently when the products of reaction could not escape both reactions took place. We express the facts thus:

$$Fe_3O_4 + 4\ H_2 \leftrightarrows 3\ Fe + 4\ H_2O, \tag{3}$$

and call it a ***reversible reaction.*** In equation (1) the steady flow of hydrogen swept the steam out of the tube before it had a fair chance to react with the iron. In equation (2) the steady flow of steam swept the hydrogen out of the tube before it had a fair chance to react with the oxide. But in a closed tube every possible reaction has a chance because nothing escapes; the four substances remain in good contact. It appears, then, that chemical affinity alone is not sufficient to explain all reactions. The conditions of reaction are important. Many reversible reactions can be made to proceed to completion by any scheme for removing one of the products or turning it into something inactive. The escape of a gas or the formation of an insoluble precipitate prevents reversal. There is comparatively little contact with precipitates. Some reactions are not reversed even if good contact is secured. An example follows:

$$2\ KClO_3 \rightarrow 2\ KCl + 3\ O_2.$$

In any reversible reaction like that represented by equation (3) the two opposing reactions adjust their speeds until equal; and a condition of equilibrium is reached when there is no further change in the relative quantities of the reacting substances. Of course any change in the conditions such as temperature, etc., will disturb this equilibrium to the right or left by favoring one reaction more than the other. A new equilibrium is soon reached. For example, in a sealed tube containing iron and water when equilibrium is reached at 200° there are twenty volumes of steam to one of hydrogen, but at 440° only six volumes of steam to one of hydrogen, and at 1500° the volumes are equal.

In Brin's oxygen process as originally used the effect of a temperature shift on the equilibrium was utilized:

$$2\ BaO + O_2 \rightleftarrows 2\ BaO_2.$$

Barium monoxide was heated in air to 500° C. and the reaction proceeded to the right. Then it was heated to 1000° and the action was reversed, thus making oxygen available unmixed with nitrogen from the air. Obviously as the temperature rose both reactions took place simultaneously.

Exercise 4. — Is the manufacture of ozone an example of a reversible reaction?

Exercise 5. — Why does the reaction between iron and hydrochloric acid proceed to completion although under proper conditions hydrogen reacts with the ferrous chloride formed?

$$Fe + 2\ HCl \rightarrow FeCl_2 + H_2.$$

To make the subject of equilibrium clear by the use of a ridiculous illustration, let us imagine a large heap of gold dollars on the ground beneath the classroom window. The Freshman class arrives with shovels and awaits the signal to throw the money in through the window to the waiting Sophomores, also equipped with shovels. During the first minute of the contest the coins fly into the room at a high rate of speed, perhaps ten thousand a minute. Why not: with plenty of opportunity for each shovel to get at the big pile? During that first minute the impatient Sophomores in the room cannot acquire much speed, not for lack of willingness, but for lack of money to work on. Their outward velocity is perhaps two thousand dollars a minute. In the next minute the Sophomores have a better chance, for more money has come in, and soon every man is busy and the outward velocity steadily increasing. But outside the big heap of money diminishes rapidly, thanks to the unhampered opportunity for work. Soon, however, there is less opportunity for each Freshman on the ground to get at the dwindling heap, and as a result the inbound velocity decreases. What is the end of this contest in which one rate of flow increases while the counter flow decreases? Obviously there comes a time when the two velocities are equal and just as much money flies into the window as out. Thereafter there is no change in the size of the two heaps of coins, although everybody is busy and money continues to fly. Equilibrium has been reached.

The student will remember the principle of reversible reactions better by the use of this absurd illustration than by dealing only with iron oxide and hydrogen. The end justifies the means.

Exercise 6. — Remembering that liquid water turns into gaseous water, that is, evaporates, give the equilibrium discussion as applied to a stoppered bottle partly filled with water.

When the stopper is removed, what happens?

Uses of Hydrogen. — Hydrogen manufacture is no longer a negligible industry. For many years this gas has been used in the oxyhydrogen blowpipe to weld metals or cut up large masses of scrap iron. As mentioned before, it has a large and growing use in hardening fats. Cottonseed oil, for example, is a liquid fat, but if hydrogen under some pressure is passed through it in the presence of finely divided nickel, the hydrogen adds directly to the fat molecules, forming a new substance, also a fat, but a solid. "Crisco," and similar substitutes for lard in cooking, are made this way. Some liquid fats are decomposed to yield liquid acids which are hardened in the same way to form solids suitable for use in candles. The enormous military use of hydrogen in balloons and Zeppelins continues as a peace enterprise. One liter of hydrogen weighs 0.09 g., but one liter of air weighs 1.29 g. Hence the lifting power of a liter of hydrogen is the difference, or 1.2 g. under ordinary conditions.

Exercise 7. — The largest dirigible yet built, the R-38, holds 2,724,000 cubic feet of gas. Calculate its lifting power from the buoyant effect of a liter, as just given. In the Appendix is a table giving the number of liters in a cubic foot.

The Activity Series of Metals. — We have already noted that sodium and potassium violently displace hydrogen from cold water, that calcium does so at moderate speed, that magnesium reacts noticeably with boiling water, that red-hot iron reacts with steam, and that copper and platinum do not react with water under any conditions. We have also noticed that magnesium and aluminum displace hydrogen from a dilute acid with much greater speed than does zinc or iron. Furthermore we have learned that copper and gold and platinum do not displace hydrogen at all from acids. These, and other facts, enable us to write the metals in the order of their activity, the most active at the top.

Potassium
Sodium
Barium
Strontium
Calcium
Magnesium
Aluminum
Manganese
Zinc
Cadmium
Iron
Nickel
Tin
Lead
Hydrogen
Copper
Mercury
Silver
Platinum
Gold

Silver and the metals below it do not unite directly with oxygen, but the farther above silver a metal is, the more vigorously it unites with oxygen. Since the metals below hydrogen do not displace hydrogen from the carbonic acid of natural waters, they are the only ones found free as minerals. The higher in the series a metal is placed the more difficult it is to reduce its oxide with hot hydrogen. This means that the more active elements form the more stable compounds. For example, the oxides of the "noble" metals, such as mercury, are unstable on heating.

How to Solve Problems. — Suppose we solve a problem as an example of an almost infallible method.

How many grams of hydrogen are formed when 80 grams of zinc react with sufficient hydrochloric acid to dissolve the metal?

I. Write the equation:

$$Zn + 2\ HCl \rightarrow H_2 + ZnCl_2.$$

II. Select the two substances that are being discussed. From the equation we learn how many atoms or molecules are being compared.

$$\text{Zn}\left\{\begin{matrix}\\ \\ \\ \end{matrix}\right.$$

$$2\ \text{H}\left\{\begin{matrix}\\ \\ \\ \end{matrix}\right.$$

(We balanced the equation solely to learn that one atom of zinc and two atoms of hydrogen were being compared. We are not concerned with the amount of HCl provided there is enough to react with all the Zn, nor does the problem ask anything about the $ZnCl_2$.)

III. Write down four numerical values, two in grams, etc., and two in terms of atomic weights. Of course, the value to be found is x grams, etc.

$$\text{Zn}\begin{cases} 80\ \text{g.} \\ 65.4 \end{cases}$$

$$2\ \text{H}\begin{cases} x\ g. \\ 2.01 \end{cases}$$

(A common error here is to write down the atomic (or molecular) weights of the two substances, but note that we are comparing the weights of *one* atom of zinc and *two* atoms of hydrogen.)

IV. Write these four values in a chemical proportion. Any value will do for the first term, but the first and second must use the same units as grams-grams or atomic weights-atomic weights, while the first and third terms must refer to the same substance. Label the terms and solve for x.

g. of Zinc : g. of Hydrogen = Wt. of Zn : Wt. of 2 H
$80 : x = 65.4 : 2.01$
$x = 2.46$ grams of hydrogen.

If this method is followed closely mistakes will be rare. Had liters of hydrogen been asked for, the 2.46 g. could be converted into liters after learning the weight of one liter.

Exercise 8. — 11.2 liters of hydrogen are passed through a heated tube containing dry copper oxide. What weight of water could be condensed beyond the heated tube?

Exercise 9. — How many liters of hydrogen can be released from water by 80 g. of calcium?

Exercise 10. — How many grams of iron will be required to release 100 g. of hydrogen from sulfuric acid?

Exercise 11. — How many grams of sulfuric acid will exactly react with 48 grams of aluminum?

Exercise 12. — Compare hydrogen and oxygen in several properties.

Exercise 13. — Will silver react with hydrochloric acid?

Exercise 14. — Will gold rust or burn?

Exercise 15. — Calculate the percentage of oxygen in potassium chlorate.

Exercise 16. — How many grams of oxygen are in 1 Kg. of potassium chlorate?

Suggestions for Review

Ten minutes' questioning of yourself on the things brought out in the lecture if given within two hours is worth an hour's review the next day.

In all equations underline the formulas for insoluble products. Use an arrow pointing upward (↑) to indicate the escape of gases formed.

CHAPTER V

VALENCE

Valence is most easily understood by reasoning from experiment. If we weigh out the metals sodium, magnesium and aluminum in proportion to their atomic weights, we should take 23 g. Na, 24 g. Mg and 27 g. Al. For that matter 23 tons Na, 24 tons Mg and 27 tons Al would maintain the same proportion. As a matter of convenience it is better to weigh out 23 mg. Na, etc.

It is of vital importance here to know that a "gram-atomic weight" of sodium (23 g.), a gram-atomic weight of magnesium (24 g.) and a gram-atomic weight of aluminum (27 g.) all contain the same number of atoms. If this is not clear, imagine that French soldiers average 150 lb. and German soldiers 160 lb. Calculate the number of soldiers in a detachment of Germans with a total weight of 160,000 lb. and in a detachment of French with a total weight of 150,000 lb. Evidently there are 1000 men in each detachment. We weighed out both groups in proportion to the weights of the individuals.

Suppose, then, that we weigh out 23 mg. of sodium, 24 mg.[1] magnesium and 27 mg. of aluminum and introduce them under inverted tubes (Fig. 25) of dilute hydrochloric acid (a solution of HCl in water). After the hydrogen released has displaced water from the tubes into the beaker of water below, the tubes are adjusted until the levels of water inside and out are the same. Making the usual corrections for pressure, temperature and presence of water vapor, the results are as follows:

23 mg. sodium	released 11 cc. hydrogen = 1 mg.
24 mg. magnesium	released 22 cc. hydrogen = 2 mg.
27 mg. aluminum	released 33 cc. hydrogen = 3 mg.

---

[1] In practice it is best to put the fresh cut sodium in a small gelatin capsule. In a few minutes the capsule is dissolved and the water comes in contact with the sodium. Magnesium ribbon should be cleaned with sand-paper and aluminum etched with dilute base, washed and dried before weighing.

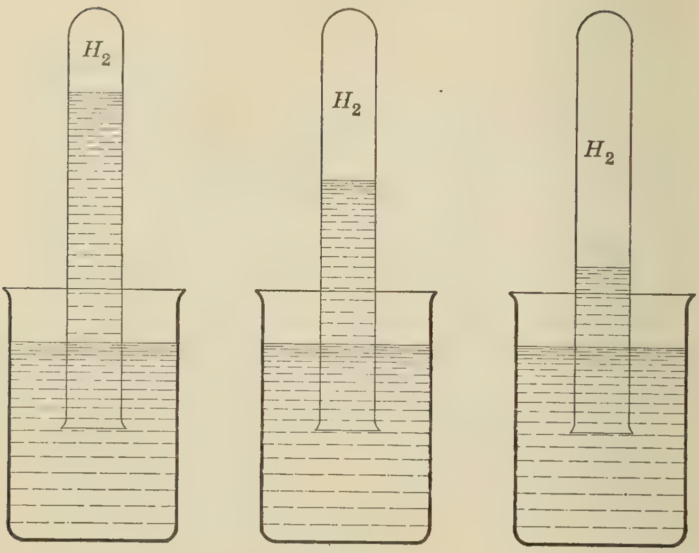


FIG. 25

(From the weight of 1000 cc. of hydrogen, 0.09 g., the weight of 11 cc. or any other volume can be calculated by proportion.)

From the above results we see that one atomic weight of sodium *in milligrams* released exactly one atomic weight of hydrogen in milligrams, while one atomic weight of magnesium in milligrams released *two* atomic weights of hydrogen in milligrams, and one atomic weight of aluminum in milligrams released *three* atomic weights of hydrogen in milligrams.

By using the *atomic weight* of each metal in milligrams we knew we were using equal numbers of atoms. The above results can then be expressed as:

1 atom of sodium	displaced 1 atom of hydrogen
1 atom of magnesium	displaced 2 atoms of hydrogen
1 atom of aluminum	displaced 3 atoms of hydrogen

$$\mathrm{Na}+\mathrm{HCl} \rightarrow \mathrm{NaCl}+\mathrm{H}$$
$$\mathrm{Mg}+2\ \mathrm{HCl} \rightarrow \mathrm{MgCl_2}+2\ \mathrm{H}$$
$$\mathrm{Al}+3\ \mathrm{HCl} \rightarrow \mathrm{AlCl_3}+3\ \mathrm{H}$$

Not merely does one atom of sodium displace one atom of hydrogen, but in the resulting compound, sodium chloride, it holds one atom of chlorine. To be sure that was just what one atom of hydrogen did in a molecule of hydrogen chloride (HCl). We see that the displacing capacity (towards hydrogen) and the holding capacity (towards chlorine) are twice as great with magnesium and three times as great with aluminum as with sodium. We call this capacity ***valence*** and define as "univalent" any element one atom of which displaces or holds one atom of hydrogen or holds one atom of chlorine. Of course one atom of a bivalent element could displace two atoms of hydrogen or hold two atoms of chlorine. Magnesium must be bivalent and aluminum trivalent. Oxygen, as shown by the formula H_2O, must have a valence of two, since one atom holds two atoms of univalent hydrogen. CaO is the accepted formula for quicklime, calcium oxide. Since we have just reasoned that the valence of oxygen is two, we now have a logical right to state that the valence of calcium is also two, for one atom of calcium holds one atom of divalent oxygen. A common error at this point is the incorrect statement that any *element* one atom of which holds just one atom of any other element is univalent.

Exercise 1. — According to the formulas HCl, H_2O, NH_3, and CH_4 what do we know of the valence of chlorine, oxygen, nitrogen and carbon?

We have just learned by experiment that the valence of aluminum is three. And since oxygen is bivalent the correct formula for aluminum oxide must be Al_2O_3. The total valence of the two aluminum atoms is six, which equals, as it should, the total valence, six, of the three oxygen atoms.

Exercise 2. — What must be the correct formula of magnesium oxide? Of calcium chloride? Of sodium oxide?

It must be admitted that some elements have two or more valences, but most have only one. In red cuprous oxide, Cu_2O, the copper is univalent, for it takes two atoms of it to hold one bivalent oxygen. In black cupric oxide, CuO, the copper is bivalent, for one atom holds one atom of bivalent oxygen. In the two chlorides of iron, $FeCl_2$ and $FeCl_3$, ferrous and ferric chlorides, we have another illustration of variable valence. Nitrogen in its five oxides, N_2O, NO, N_2O_3, NO_2, N_2O_5, shows different valences. But when an element has more than one valence it is a comfort to remember that in most cases only one is common. The usual valence of copper is two.

Radicals. — We have already noticed in equations such as

$$2\ Na + H_2SO_4 \rightarrow Na_2SO_4 + H_2$$
$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$
$$2\ Al + 3\ H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3\ H_2$$
$$BaCl_2 + Na_2SO_4 \rightarrow BaSO_4 + 2\ NaCl$$

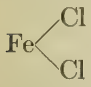
that one sulfur atom and four oxygen atoms seem to hold together as a group or *radical* during reactions, passing from one compound to another unchanged, much as a family of Arabs might move from one tribe to another without the loss of any of its units, parents or children. We call the SO_4 group of atoms the "sulfate radical." It is incapable of existing alone and its compounds are always called "sulfates." For example, H_2SO_4 is always known as "sulfuric acid," but it could be called "hydrogen sulfate." Sodium sulfate is Na_2SO_4, magnesium sulfate is $MgSO_4$, and aluminum sulfate is $Al_2(SO_4)_3$. In nitric acid, HNO_3, and the nitrates derived from it such as $NaNO_3$ and $Cu(NO_3)_2$, we find the NO_3 group of atoms holding together pretty well through all sorts of reactions, so we call it the "nitrate radical." In phosphoric acid, H_3PO_4, and the phosphates made from it such as Na_3PO_4, we see a similar group — PO_4 — called the "phosphate radical." These radicals have valence. Thus in HNO_3 a single nitrate radical holds one univalent hydrogen; in H_2SO_4 the sulfate radical plainly holds two hydrogens; in H_3PO_4 the phosphate radical holds three hydrogens. The natural assumption is that the nitrate radical is univalent, the sulfate radical bivalent, and the phosphate radical trivalent. We can easily learn the valence of any acid radical by looking up the correct formula of the corresponding acid and counting the hydrogen atoms held by one radical. A knowledge of the valence of radicals is very convenient in remembering correct formula. For example, $CuSO_4$ must be the correct formula for copper sulfate (blue vitriol) because we know already that copper is bivalent (see CuO) and so is the sulfate radical (see H_2SO_4). Therefore the two valences just exactly hold each other, as they should in all compounds. $Al_2(SO_4)_3$ must be the correct formula for aluminum sulfate because the valence of aluminum is three (see $AlCl_3$) and of the sulfate radical two. Therefore $AlSO_4$ cannot be right, because a valence of three for the metals is not equal to a valence of two for the radical. Two aluminum atoms furnish a total of six (2 × 3), just equaled by the total valence six (3 × 2) of the three sulfate radicals. It is a great help to put dots above the elements or radicals, as in $CaCl_2$ or $Al(SO_4)_3$ or $Cu(NO_3)_2$ to indicate their valence.

Exercise 3. — You have already learned from the original experiment that H', Na', Cl', Mg'', Al''' are correct and you have logically proved the correctness of Ca'', Cu'', Ba'', N''', C'''' O'', SO_4'', NO_3' and PO_4'''. Now correct the following formulas *when necessary.*

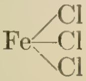
$CaPO_4$
HPO_4
$NaPO_4$
$Mg(PO_4)_3$
$BaPO_4$
$CuCl_3$
Ba_2O
HNO_3
$Al(NO_3)$
$BaNO_3$
$CaCl$
$Mg(NO_3)$
$Al(SO_4)$
$Na(NO_3)$
NH

Note: A very quick method of learning the valence of a new element is to use the "Index" of the text. There a reference may be found to a page where the correct formula of the oxide or chloride is given.

Structural Formula. — It is convenient to represent the valence between elements by straight lines or "bonds of valence." Thus Na-Cl is the structural formula for sodium chloride (common salt). Since the valence of sodium is one and also one for chlorine, this single line is a convenient picture of the relation.

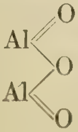


and

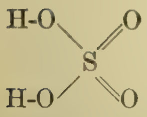


represent ferrous chloride and ferric chloride, in which iron is seen to have valences of two and three. The "-ic" compounds of a metal are those in which the metal has a higher valence than the "-ous" compounds.

The formula



merely represents Al_2O_3, showing the usual valences of three for aluminum and two for oxygen.



is the structural formula for sulfuric acid. The memory need not be burdened with this at present. An annoying question that will not down in the student's mind is this:

"What is the valence of the sulfur inside the -SO_4 radical?" And it is a further cause of disquiet that the student already knows that four oxygen atoms have a total valence of *eight*, yet he is told the valence of the whole group is only *two!*

The subject will be discussed later in the light of new developments.

Valence and Equivalent Weights. — Remembering that the equivalent weight of an element is the number of grams of it that combine with 1.008 grams of hydrogen or 8 grams of oxygen, we can now see a peculiar relation between valence and atomic weights. The atomic weight of aluminum is 27 and its valence 3. Now $27 \div 3 = 9$, the equivalent weight. In the case of sodium both the atomic and equivalent weights are 23, but the valence is 1. This relation holds for all. *The equivalent weight of an element may be defined as the atomic weight divided by the valence.*

A glance at the structural formula of sulfuric acid shows us that the sulfur atom and the four oxygen atoms of the SO_4 radical are well occupied in holding each other. Their effective outside valence toward hydrogen or other atoms is only two.

CHAPTER VI

WATER AND HYDROGEN PEROXIDE

WATER

History. — Cavendish, not content with his pioneering study of the properties of hydrogen, added to his laurels by synthesizing water by burning hydrogen in air and in oxygen. Lavoisier decomposed water with red-hot iron and clearly interpreted Cavendish's experiments. In 1800 Nicholson and Carlisle decomposed water into its elements by electrolysis.

Occurrence. — Water is the most essential and most abundant compound. Three fourths of the earth's surface is covered with water, and in the form of vapor it is an indispensable part of the atmosphere. It makes up two thirds of the human body. In fact there is truth as well as humor in the description of a man as "twelve pounds of ashes and eight buckets of water." Plant tissue contains from 50 to 75% water. Evidently moisture in the soil and in the air are necessary to plant life. Water evaporates from the oceans, rivers and lakes or, in other words, turns into the gaseous state. In this form it is carried over the land and, when sufficiently cooled in the upper air, falls as rain. Thanks to the sun's heat aiding evaporation and to the wind currents, this process is repeated indefinitely. A cubic mile of air can hold so much moisture on a very hot day that if suddenly cooled to freezing it would precipitate 140,000 tons of water.

Physical Properties. — Pure water is colorless in thin layers, but in thick layers is blue. However we do not find absolutely pure water in nature. Fine suspended material of a yellowish tint, or light reflected from the yellow sand of a river bottom, must modify the natural blue to green. No wonder the ocean and deep lakes seem blue or green. Pure water is odorless, yet from some springs offensive hydrogen sulfide water flows. Pure water is also tasteless; in other words it tastes "flat." The pleasant taste of good drinking water is due to dissolved air and carbon dioxide. This explains why boiled water is so unpalatable.

One cubic centimeter of water at 4° C. weighs one gram, so by definition its ***density*** is one. It expands on warming above or cooling below this point. A fortunate thing it is that ice is lighter than water. Otherwise as fast as the water on the surface of a river or lake froze it would sink and the lake would soon be solid to the bottom. In deep waters the summer sun would accomplish little. Fish would become extinct in a single winter. The ***specific heat*** of water is 1, which means that it requires one calorie of heat to raise one gram of water one degree. This is greater than the specific heat of any other substance. It is for this we prize a hot-water bottle — at times — and enjoy a hot-water heating system. Since the specific heat of many common rocks is only one fifth that of water, it is evident that great bodies of water heat up slowly and cool off slowly in comparison with land, thus moderating climatic changes.

Under 760 mm. pressure liquid water becomes solid ice at 0° C. and gaseous steam at 100° C. In melting one gram of ice at 0° C. into water at 0° C. 79 calories of heat must be absorbed. Conversely, on freezing one gram of water releases 79 calories. This is called the ***heat of fusion of ice.***

A mixture of water and ice maintains a temperature of 0° C., but water alone can be supercooled below 0° C. without turning solid if it is not stirred or brought in contact with a fragment of ice as a "starter." So the freezing point is the temperature of a well-stirred mixture of ice and water.

One gram of water at 100° C. requires 540 calories of heat to change into steam at 100° C. On condensing this steam into water, the same 540 calories of heat — the ***heat of vaporization*** — are released. No wonder steam is so efficient in heating houses. It takes a great deal of heat to "raise steam" in the boiler, but we get it back in the radiators, which are merely convenient steam condensers.

Chemical Properties. — When heated at 1000° water begins to *dissociate* or break down into hydrogen and oxygen. At 2000° 1.8% has dissociated. Of course the two elements are recombining all the time, and at each new temperature a new equilibrium is found.

At 2000° $H_2+O \leftrightarrows H_2O$

$1.8\% \qquad 98.2\%$

Exercise 1. — Can any other form of energy than heat be used to decompose water?

The following may be as much a physical as chemical property; but however that may be, it is of fundamental importance. Water is the greatest catalyst we have. Ordinarily we merely say that it aids reaction. Two substances very intimately mixed (dissolved) in water are in better contact than is possible without the water, and then there is another helpful effect to be discussed later (see Ionization). Many reactions, perhaps all, require at least a minute trace of moisture. A mixture of absolutely dry oxygen and hydrogen cannot be exploded.

Water reacts with some elements such as chlorine and sodium:

$$Cl_2 + H_2O \leftrightarrows HCl + HClO,$$
$$2\,Na + 2\,H_2O \rightarrow 2\,NaOH + H_2.$$

Exercise 2. — What metals react with cold water? What metals react only when very hot? Can carbon be made to react with water?

Water reacts with many compounds. The student will recall from the oxygen experiments that when phosphorus burned in a jar of oxygen to form an oxide (P_2O_5) this was shaken with water. The reddening of blue litmus paper showed that an acid was formed.

$$P_2O_5 + 3\,H_2O \rightarrow 2\,H_3PO_4$$
$$SO_2 + H_2O \rightarrow H_2SO_3$$
$$CO_2 + H_2O \rightarrow H_2CO_3$$

In all the above cases acids were formed, but the oxides of calcium and sodium yielded very different products with water. The solution turned litmus blue. Bases were formed:

$$Na_2O + H_2O \rightarrow 2\,NaOH,$$
$$CaO + H_2O \rightarrow Ca(OH)_2.$$

The elements whose oxides react with water to form bases are called *metals* and the elements whose oxides react with water to form acids are called *non-metals*. This differs from the popular conception of metals, but there is no occasion for alarm. The common metals are still included in the list of metallic elements.

Water also reacts with ammonia gas to form the soluble base, ammonium hydroxide:

$$NH_3 + H_2O \leftrightarrows NH_4OH.$$

Hydrates. — Certain substances crystallize out from their water solutions on slow evaporation of the liquid, carrying definite amounts of the water with them. This ***water of crystallization,*** as it is called, is not held in a wet sponge fashion, for no amount of pressure will squeeze it out. Moreover a sponge can hold any amount of water, within wide limits. Not so these ***hydrates*** which we are discussing. These are chemical compounds with definite amounts of water. Some substances, it is true, can crystallize with two or three definite amounts of water, but the shape of the crystals, solubility, and some other properties are then different. These hydrates feel dry to the touch but easily lose their combined water on heating. On adding the heated product to water the same solution is obtained as if the crystals had been used. For example, blue vitriol is a hydrate with five molecules of water of crystallization, $CuSO_4 . 5\,H_2O$. When heated above 200° all the water is lost and a white powder is obtained, $CuSO_4$. Under favorable conditions this can be obtained in crystals of a different shape. But add either $CuSO_4 . 5\,H_2O$ or $CuSO_4$ to water and the same blue solution results in either case. On careful evaporation of the two solutions both produce blue crystals of $CuSO_4 . 5\,H_2O$:

$$CuSO_4 + 5\,H_2O \rightarrow CuSO_4 . 5\,H_2O.$$

This equation represents the formation of blue vitriol. We should note, in passing, the distinction between hydrates and hydroxides. Take, for example, those substances, either acids or bases, which are called *hydroxides:*

$$CaO + H_2O \rightarrow Ca(OH)_2,$$
$$CO_2 + H_2O \rightarrow H_2CO_3.$$

Some hydroxides, like hydrates, lose water readily on heating. Silver hydroxide loses water as fast as it is formed at ordinary temperatures, so that we secure only silver oxide. In fact the oxide may be drowned with water, but it refuses to hold any of it.

We noted in a previous chapter that a few drops of water let into the vacuum at the top of a barometer forced the mercury down several millimeters, an increasing distance with rise in temperature. This pressure, called ***vapor tension,*** is merely the partial pressure of water vapor. Now if instead of drops of water a crystal of sodium sulfate, $Na_2SO_4 . 10\,H_2O$, be introduced into the barometer tube, the mercury falls almost as much as for water itself and the clear crystal crumbles to a white powder. Some other hydrates depress the mercury less. The depression in millimeters is a measure of the tendency of the water of crystallization (or water of hydration) to evaporate. Place a clean crystal of $Na_2SO_4 . 10\ H_2O$ in the open air and it soon crumbles to a white powder weighing far less. Evidently the outward pressure (aqueous tension) of the water in the crystal is greater than the back pressure of water vapor in the air. Such loss of water from hydrates is called *efflorescence*. Washing soda, $Na_2CO_3 . 10\ H_2O$, acts in similar manner. Other hydrates lose little or none of their water in air, blue vitriol, for example. This means that the aqueous tension of $CuSO_4 . 5\ H_2O$ is about the same as that of ordinary air. But in absolutely dry air blue vitriol would lose water. There are some very soluble substances of low vapor tension such as calcium chloride which become wet in ordinary air. Such substances are *deliquescent*. They dissolve in the film of moisture on their surface, forming a concentrated solution of lower vapor tension than the air. Consequently moisture is deposited in the solution, tending to dilute it. This explains the use of anhydrous calcium chloride as a drying agent to take up moisture from gases.

It is in order here to remark that a great many substances attract and hold a film of moisture on their surface. In the case of fine powders with enormous surface this becomes quite noticeable. In very accurate weighing we allow for the increase in weight of a glass vessel or porcelain crucible due to this film of moisture. Our procedure is to put the vessel in a *desiccator* which is merely a glass box with a very deliquescent substance (calcium chloride, for example) on the bottom. The air in the desiccator is dry and so the little moisture we introduce quickly evaporates and is taken up by the drier.

The Boiling Point of Water. — Water in an open vessel boils when its aqueous tension equals the pressure of the air as stated on page 42. Then with violent bubbling and breaking of its surface it changes into steam. The boiling point of water is 100° when the air pressure is 760 mm., but on top of Mt. Blanc water boils at 84.4° because the pressure averages 424 mm. So we understand why campers on a high plateau might boil potatoes to the limit of patience without any nutritious result. It is temperature that cooks potatoes and other foods, not the mere violent ebullition we call boiling. If we evacuate the air from a bell jar containing a beaker of cold water, the water boils violently because its aqueous tension at last equals the decreased pressure of the air. Pressure cookers are great aids in the speedy and economical cooking of tough meats. With a lid clamped on tightly the steam soon raises the pressure so that the boiling point of the liquid present is raised. In other words the meat can get hotter than in an open vessel under a pressure of one atmosphere.

Exercise 3. — How does a hydrate differ from a solution or from a hydroxide?

Exercise 4. — If water vapor above the mercury in a barometer tube were heated to 100°, how high a column of mercury would still remain below it? It is understood that sufficient excess of water is present to keep the vapor saturated.

Natural Waters. — Water is the most nearly universal solvent we have. Most substances are dissolved by it to at least a minute extent. Even glass beakers are not proof against its action. If we add a drop of phenolphthalein solution to water in a glass vessel, no color is to be seen. If we now add glass powder with its vastly increased surface, the water turns pink, due to the solution of part of the glass and a resulting reaction with phenolphthalein.

Is it any wonder then that rain water dissolves rock material and gradually carries it to the sea? Freezing, with its expansion of water in crevices, disintegrates rock and is aided by the force of waves and currents. But for such wonderful provisions of nature our soil would be a barren rock.

Among the rocks most easily dissolved are the carbonates of calcium and magnesium known as limestone and dolomite. Water containing a little carbon dioxide from the air is particularly effective. For this reason the water in limestone regions is very "hard." This hardness is not dangerous to health, in fact some think it healthful, but it causes great loss of soap in washing and a great waste of heat in boilers by causing the formation of boiler scale. We often try to remove much of this hardness by adding chemicals to soften the water. The important subject of water softening will be taken up in detail when we study calcium.

It is not merely rock material that is contained in the water of wells, springs, lakes and streams. Rain water washing the surface of the ground dissolves dead plant material and animal refuse, sometimes to such an extent as to give a brownish color and slight odor and taste. But the worst feature of this "carry-all" nature of water is its ability to pick up bacteria that cause disease, typhoid, for example. Two men camped one winter on a watershed that supplied water for a small town reservoir. One fell ill of typhoid and the other nursed him for several weeks. As soon as the ground thawed and the house refuse was washed into the reservoir an epidemic of typhoid broke out in the town. Of course sewage should never be allowed to contaminate drinking water in such direct fashion.

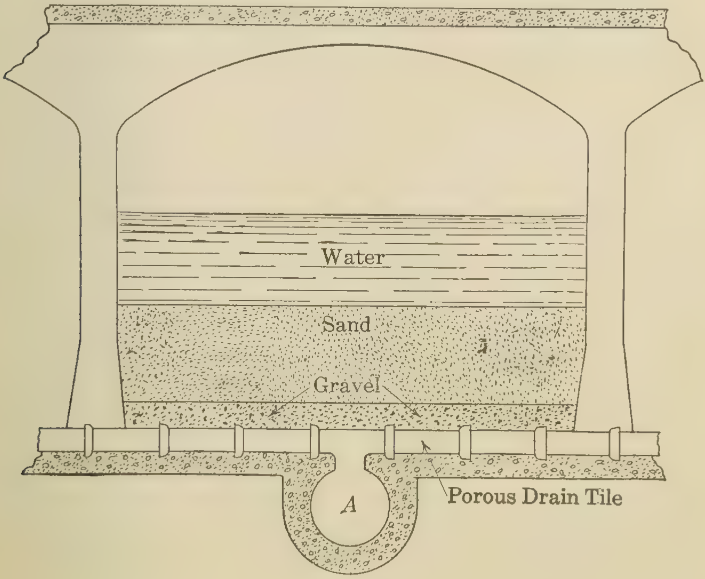


Fig. 26

Purification of Water. — Dangerous bacteria in drinking water may be killed by small amounts of chlorine. This gas is soluble in water, so mixing is simple. Many great cities treat their water supply in this way. If too much chlorine be added a slightly unpleasant taste is noticed, but this excess is not necessary. Bleaching powder, a chlorine product, is about as effective as chlorine.

In Europe over a hundred cities purify their water with ozone *after* filtering and settling. Ozone kills bacteria and leaves no unpleasant taste no matter how much is used. However it is more expensive than chlorine and is not so dependable in operation.

One of the latest developments is the use of ultraviolet light which kills bacteria instantly if the water is perfectly clear. This light is produced by the mercury vapor lamp when made of clear quartz tubes. Some special arc lights throw out these rays in considerable strength. The cost and difficulty of installation make this a method suited only to expensive houses and hotels.

The universal method of treatment is sand filtration (Fig. 26). Nearly all city filters are built up of a layer of gravel covered by coarse sand, and then a layer of finer sand several feet deep in all. Now bacteria are so small that they are seen only by the aid of the highest powered microscopes, so it is absurd to imagine that they are too large to pass between the sand grains. We can see the spaces between sand grains with the naked eye. But the facts are that a good sand filter not only catches mud but catches practically all the bacteria. The explanation is simple. The surface of each sand grain has an attraction toward bacteria and *adsorbs* them. This is a common phenomenon. Most surfaces have such an attractive power towards some other substances. After a sand filter has been used a slimy growth develops on the top, products of bacterial action, and this has a still greater adsorptive power towards bacteria than sand itself. The best American practice is to let muddy river water settle in large basins before filtering. This saves the filter from too great a load of mud. The water is sometimes sprayed into the air to give oxygen a chance to oxidize some of the impurities.

Many small towns and even larger cities (Columbus, Ohio, is a notable example) soften their water supply by adding lime, soda, and, at times, alum. The precipitate formed drags down nearly all the bacteria on settling, so both softening and purifying are accomplished in one operation.

Pure drinking water may be obtained by distillation (Fig. 27), but the distillate has a "flat" taste, due to the lack of air and carbon dioxide.

In the Spanish-American War, lack of sanitary precautions led to a greater loss of life in the army than that due to fighting. A great part of this loss was due to the entrance of typhoid bacteria into the camp water. In the Great War our army benefited greatly by extreme care in the supply of pure drinking water. Whipple says that records kept in twelve of our greatest states show that the deaths from typhoid in 1880 were 55 per 100,000 population and in 1910 only 19 per 100,000. This improvement was wholly due to purification of drinking water. The old-fashioned idea that clear, sparkling, palatable water must be pure has been exploded. It may be as dangerous as a cup of poison if it carries the germs of typhoid.

A classical illustration is the Hamburg-Altona record. Altona is just below Hamburg on the Elbe river in Germany. Hamburg, in 1892, did not filter the water, while Altona took that precaution. Hamburg's death rate from typhoid was over six times that of Altona. The two cities really merged, so on one street the Hamburg side was stricken with typhoid, while the Altona side was nearly free from it.

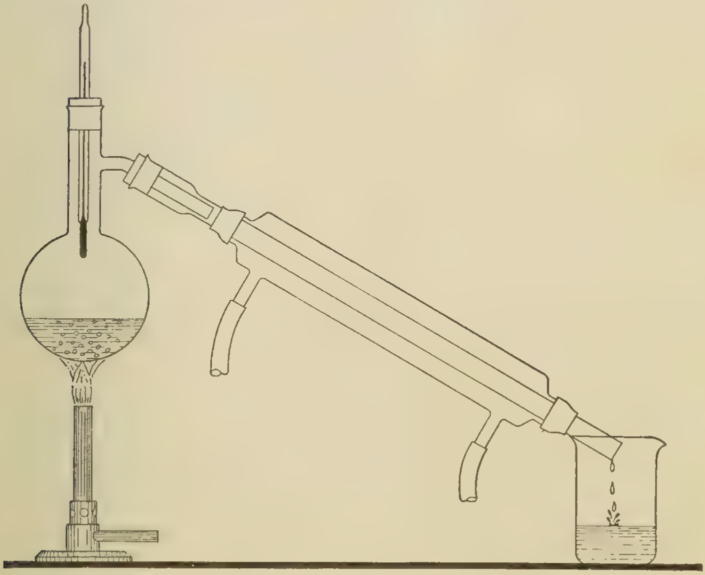


FIG. 27

Chicago once dumped its sewage into Lake Michigan and drew its city water from the same lake. Finally the Chicago river was deepened and its current reversed into the Mississippi system, thus making the river a sewage canal. The death rate from typhoid quickly fell from 170 per 100,000 to 16 per 100,000.

HYDROGEN PEROXIDE

Hydrogen peroxide resembles ozone in its "safe and sane" oxidizing action on delicate materials. These two gases are often studied together. Traces of hydrogen peroxide are found in the air, probably formed by the action of the ultraviolet rays of the sun acting on moist oxygen. The occurrence in air was proved by catching the moisture condensed on the outside of a bottle of ice and applying an extremely delicate test to this water. We buy hydrogen peroxide as a 3 per cent solution in water.

Preparation. — When the flame of an oxyhydrogen blowpipe impinges on floating ice in a vessel of water, traces of hydrogen peroxide can be found in the water. It is probably formed, in traces at least, when any substance, ether for example, is oxidized in the presence of moisture. In most cases it is decomposed at once.

A convenient laboratory method of preparation is to drop sodium peroxide slowly into ice water:

$$Na_2O_2+2\ H_2O \leftrightarrows H_2O_2+2\ NaOH.$$

If too much sodium peroxide be added too rapidly the heat of reaction decomposes the product desired into water and oxygen. The following reactions may also be used in preparation of this compound:

$$(1)\ Na_2O_2+H_2SO_4 \rightarrow H_2O_2+Na_2SO_4,$$
$$(2)\ BaO_2+H_2SO_4 \rightarrow H_2O_2+BaSO_4,$$
$$(3)\ BaO_2+H_2CO_3 \rightarrow H_2O_2+BaCO_3,$$
$$(4)\ 3\ BaO_2+2\ H_3PO_4 \rightarrow 3\ H_2O_2+Ba_3(PO_4)_2,$$
$$(5)\ BaO_2+2\ HCl \rightarrow H_2O_2+BaCl_2.$$

Reaction (2) is the one favored commercially. The barium sulfate, being insoluble, is filtered off. In fact reactions (3) and (4) are good and (5) poor because barium salts are poisonous and we prefer to filter off some insoluble barium salt, leaving in the filtrate only hydrogen peroxide and water. The barium chloride of (5) is soluble, while the carbonate, phosphate, and sulfate of barium are insoluble. Sodium sulfate does no harm.

Pure hydrogen peroxide is difficult to make and almost impossible to keep. If an attempt be made to boil off the water from the usual solution the peroxide decomposes. But by boiling under diminished pressure, at 26 mm., water is removed at 69° and a syrup obtained. It explodes on almost no provocation at all. The explosiveness of hydrogen peroxide is due to the large amount of heat *released* when it decomposes. So if a little decomposes the rest gets hotter and the process is accelerated to the speed of explosion. Most things *absorb* heat on decomposing and so cool themselves off, checking reaction speed. If we add powdered manganese dioxide to commercial hydrogen peroxide, a marked rise in temperature is observed, indicating more rapid decomposition.

Properties. — Hydrogen peroxide is a colorless, odorless liquid with an astringent, bitter taste, freezing at $-2°$. At $-10°$ crystals separate. Its density at 0° is 1.46. It mixes with water in all proportions and is comparatively stable in such solutions. Light decomposes it, so brown bottles are the best containers. The trace of alkali from the glass decomposes it. A very little acid can counteract this tendency by reacting with the alkali. Usually a trace of acetanilide is used to check decomposition:

$$H_2O_2 \rightarrow H_2O + O_2.$$

The above reaction is caused by bases, finely divided gold, platinum, manganese dioxide and many other substances which are themselves unchanged, therefore acting as catalysts. Neutral salts dissolve in pure hydrogen peroxide without causing any decomposition.

The oxidizing power of hydrogen peroxide is its most valuable property. However, the action is not vigorous, and a harmless by-product, water, is formed. Hence its popularity as a gargle and for other medicinal uses. Its ability to kill bacteria, although real, has been greatly overestimated by the public. On pus and blood it reacts with effervescent release of oxygen. This gassing makes it ideal for the gentle loosening of dried bloody bandages. Its gentle oxidizing action makes it invaluable for bleaching silk, feathers, hair, ivory and various delicate materials. A darkened oil painting may be lightened by cautious use of hydrogen peroxide. Since the darkening was partly due to the formation of lead sulfide from the lead paint, the remedy is the oxidation of this dark compound to white lead sulfate:

$$PbS + 4\ H_2O_2 \rightarrow PbSO_4 + 4\ H_2O.$$

The pure anhydrous product sets fire to wood if catalyzed by a little acid.

Tests. — Like ozone, hydrogen peroxide releases free iodine from hydrogen iodide. In the presence of starch this iodine develops a blue color. A filter paper dipped in a solution of potassium iodide and starch paste (slightly acidified to release the acid) serves as a rough test, but as the oxygen of the air also releases free iodine (though slowly) from hydrogen iodide, the test is good only if a blue color forms almost instantly:

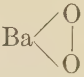
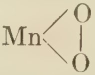
$$H_2O_2 + 2\ HI \leftrightarrows I_2 + 2\ H_2O.$$

Traces of hydrogen peroxide may be detected by the addition of dilute sulfuric acid and *very* dilute potassium dichromate ($K_2Cr_2O_7$). A blue color develops but quickly fades unless a layer of ether had been shaken quickly with the solution. The blue perchromic acid formed is more soluble in the ether layer and is stable there. Very faint colored potassium permanganate loses its pink color if hydrogen peroxide be added. This is confirmatory evidence in a test, although some other substances do the same thing. This last reaction is the basis of an important quantitative method for determining hydrogen peroxide:

$$2\ KMnO_4 + 5\ H_2O_2 + 3\ H_2SO_4 \rightarrow K_2SO_4 + 2\ MnSO_4 + 8\ H_2O + 5\ O_2.$$

This important reaction will be referred to later. Note that the oxygen gas bubbling off gets half its oxygen from the great oxidizer, potassium permanganate, and half from the hydrogen peroxide. Each oxidizer reduces the other, an unusual reaction, — somewhat like the action of two generous rich men who duplicate each other's gifts for some charity, both becoming poorer.

Exercise 5. — If a solution of potassium permanganate be just decolorized by 150 cc. of hydrogen peroxide (3 per cent by weight), how many grams of the permanganate must have been used? How many grams of oxygen escaped? Assume that the density of the hydrogen peroxide solution is practically one.

Peroxides. — The structural formula of water is H–O–H and of hydrogen peroxide H–O–O–H. Evidently sodium peroxide, Na_2O_2, is a salt derived from the feeble acid H_2O_2 by replacing the hydrogen with sodium. (This is not done directly, however.) Na–O–Na is the structural formula for this oxide. When BaO_2 is acidified H–O–O–H is formed, so  $\mathrm{Ba}<\begin{matrix}\mathrm{O}\\|\\\mathrm{O}\end{matrix}$ must represent the structure. But MnO_2 when acidified does not yield H_2O_2. Hence its structure must be O=Mn=O and not  $\mathrm{Mn}<\begin{matrix}\mathrm{O}\\|\\\mathrm{O}\end{matrix}$. Peroxides yield hydrogen peroxide when acidified and dioxides do not. MnO_2 and PbO_2 should be called dioxides.

CHAPTER VII

MOLECULAR AND ATOMIC WEIGHTS

The student has been taught to use exact atomic weights and has all along wondered how we arrived at such values. He has been promised an explanation and it is now in order.

Dalton, Gay-Lussac, Avogadro. — In 1805, just after the publication of Dalton's atomic hypothesis, Gay-Lussac found by laboratory experiment that in any chemical reaction the volumes of all gases concerned stand to each other in the ratios of small whole numbers. Avogadro in 1811 sought to explain this and other facts by his famous hypothesis that *equal volumes of all gases*, under the same conditions of temperature and pressure, *contain the same number of molecules.*

Development of Exact Weights. — From the above it is evident that if we weigh equal volumes of gases under like conditions we get weights that are in the same ratios as the weights of *single molecules.* (Read again the second paragraph in the chapter on Valence.) In other words, we can get the relative molecular weights of all gases. (Solids must be handled differently.)

If you were doing this, and know nothing of our present system of atomic and molecular weights, what gas would you naturally select as a standard with which to compare all others? You would probably select the lightest gas — hydrogen.

Since these molecular weights are only relative, what would you select as the weight of *one molecule* of hydrogen? As the lightest molecule known you would doubtless suggest "1" as the weight of a hydrogen molecule. Now the oxygen molecule actually weighs 16 times as much (1 liter of oxygen is 16 times as heavy as 1 liter of hydrogen). Therefore, on this basis (molecular weight of hydrogen = 1), the molecular weight of oxygen = 16. On the same basis the molecular weight of water vapor = 9.

Now if you analyzed water you would find that 1/9 of it is hydrogen. 1/9 of 9=1. In other words, 1 part of this molecular weight of water is due to hydrogen. Similarly 8/9 is oxygen and so 8/9 of 9=8 parts due to oxygen.

Following is a list of a few hydrogen compounds, giving molecular weights (on the basis of molecular weight of hydrogen=1) and the part due to hydrogen as shown by analysis.

A FEW OF THE MANY THOUSAND HYDROGEN COMPOUNDS

SUBSTANCE	MOLECULAR WGT.	PART OF MOL. WT. DUE TO HYDROGEN (BY ANALYSIS)
Hydrogen	1	1.0
Water Vapor	9	1.0
Hydrogen Peroxide . . .	17	1.0
Ammonia	8.5	1.5
Hydrogen Chloride . . .	18.2	0.5
Methane	8	2.0

If the complete table of many thousand hydrogen compounds were listed in this way, you would note that the smallest part of any molecule due to hydrogen was 0.5. Is it not practically certain that out of thousands of chances nature would put just one atom of hydrogen in some molecules? If so, does not the smallest amount of hydrogen (0.5) in any molecule represent the weight of one atom? Therefore should not the *atomic weight* of hydrogen be 0.5?

Now your whole system is built on the basis of the weight of a molecule of hydrogen=1,[1] which, it seemed at the start, would keep all values at "1" or above, but you have found that this results in a value of .5 for the hydrogen atom. Would it not seem more natural to start with 2 as the weight of the hydrogen molecule (the weight of the hydrogen *atom* then equals 1), and avoid needless fractions? But since the weights of molecules are relative, if you decide to double the weight of a hydrogen molecule you must double every value in the above table. Below is a list of corrected values on the basis of the molecular weight of hydrogen =2 (atomic weight=1).

---

[1] To be exact, when the atomic weight of oxygen is taken as 16, the atomic weight of hydrogen is really 1.008.

Substance	Molecular Wt.	Part of Molecular Weight due to Hydrogen
Hydrogen	2	2
Water	18	2
Hydrogen Peroxide	34	2
Ammonia	17	3
Hydrogen Chloride	36.5	1
Methane	16	4

Since the weight of one atom of hydrogen = 1, and of a hydrogen molecule = 2, there must be two atoms in that molecule and it should be represented by H_2.

In a manner similar to the above a table of thousands of oxygen compounds could be built up and the weight of an atom and a molecule determined. The same could be done for any element. It would be found that, since a liter (for example) of oxygen weighs 16 times as much as a liter of hydrogen, the molecular weight of oxygen must be $16 \times 2 = 32$. It would also be found that an atom of oxygen weighs 16 and therefore oxygen gas has the formula O_2.

Let us deduce the formula of water:—From the table, two parts of the molecular weight are due to hydrogen. Therefore there must be two atoms of hydrogen in the molecule of water. Analysis would show that 8/9 of the water molecule is oxygen. 8/9 of 18 = 16. Since the weight of one atom of oxygen = 16, there must be only one atom of oxygen in the molecule of water and the formula must be H_2O.

Exercise 1. — Deduce the formula of hydrogen peroxide in the same way.

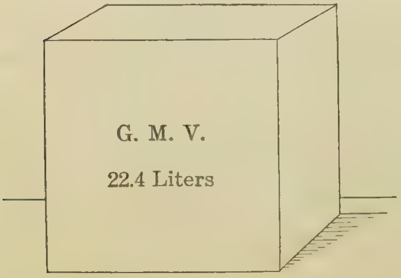


Fig. 28

The Gram Molecular Volume. — Since we have decided on 32 as the *molecular* weight of oxygen, it might be useful to know what volume the formula weight of 32 g. would occupy. One liter of oxygen weighs 1.429 g., so $\frac{32}{1.429} = 22.4$, the number of liters occupied by 32 g. of oxygen. We can, for convenience, imagine a box holding exactly 22.4 liters (Fig. 28). If it be filled with oxygen or any other gas under standard conditions, the weight of the contents in grams must be the formula weight of that gas, since that is true for oxygen. By Avogadro's law this box must hold the same number of molecules of any gas, so the weights vary as the weights of single molecules. The box filled with hydrogen weighs 2.016 g., so the molecular weight of hydrogen is 2.016. The gram molecular volume of ammonia (NH_3) weighs 17 g. Obviously the molecular weight of ammonia is 17.

In actual practice we should find it awkward to weigh 22.4 liters. We should simply weigh (get the density of) any convenient volume, perhaps 200 cc. Dumas devised this method. He used a bulb with a stopcock attached (Fig. 29). After finding the exact volume of the bulb by filling with mercury and weighing it was then weighed filled with air. Knowing the volume of air in the bulb (and the density of air) it was a simple matter to calculate the weight of the air alone. Subtracting this weight from the weight of the bulb filled with air gave the weight of the bulb alone, a method equivalent to weighing an evacuated bulb. Finally the bulb was weighed after filling with the gas whose molecular weight was desired. By subtracting the weight of the empty bulb from the weight of bulb plus this gas, the weight of the given volume of gas was found. From this it was easy to calculate, by proportion, the weight in grams of 22.4 liters. This number represented the molecular weight. Of course corrections to 0° and 760 mm. were made. A very volatile liquid can be examined by placing the bulb containing some of it in a heated water bath and when only its vapor remains closing the stopcock and weighing.

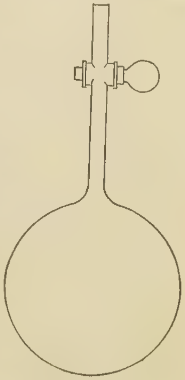


FIG. 29

EXERCISE 2. — What is the molecular weight of a gas 150 cc. of which weighed 0.235 g. under standard conditions?

EXERCISE 3. — A Dumas bulb of 300 cc. volume was filled with vapor from an easily volatilized liquid at 45°. The barometer read 740 mm. What was the molecular weight of the liquid if the gas weighs 1.25 g.?

Exercise 4. — The density of a certain gas referred to air is 1.85. (1 liter of air, standard, weighs 1.293 g.) What is the molecular weight of this gas?

Note: The weight of one liter of any gas in grams can be calculated in a minute by dividing its molecular weight by 22.4. For example, 22.4 l. of oxygen (G. M. V.) weighs 32 g. Therefore 1 liter weighs $\frac{32}{22.4}=1.429$ g.

Exercise 5. — Calculate the weight of 1 liter of nitrogen (N_2); of 300 cc. of chlorine (Cl_2); of 1500 cc. ammonia (NH_3).

Molecular Formulas. — The distinction between atoms and molecules was necessary to reconcile Gay-Lussac's law and Avogadro's hypothesis. Gay-Lussac knew that one volume of oxygen united with two volumes of hydrogen to form two volumes of steam.

$$\underset{\text{oxygen}}{\boxed{1\text{ vol.}}} + \underset{\text{hydrogen}}{\boxed{1\text{ vol.}}} + \underset{\text{hydrogen}}{\boxed{1\text{ vol.}}} \rightarrow \underset{\text{steam}}{\boxed{2\text{ vols.}}}$$

But by Avogadro's theory the two volumes of steam contained just twice as many molecules as the one volume of oxygen. Now *every* molecule of water contains *some* oxygen. There is only one way for a given number of oxygen molecules to be represented in twice that number of water molecules. Each oxygen molecule splits into two parts and each half molecule is found in each molecule of water. In other words there are two atoms of oxygen in a molecule of oxygen. A similar reasoning holds for the hydrogen. The equation above may now be written as follows:

$$O_2+H_2+H_2 \rightarrow 2\ H_2.$$

Most, but not all, *elementary* gases are diatomic. For example a molecule of chlorine is Cl_2 and nitrogen N_2. Yet mercury vapor is monatomic and its *molecular* formula is Hg. Zn is the molecular formula for zinc vapor. A few rare gases, such as helium, neon and argon, are monatomic; they are too inactive to combine with their own atoms. Temperature affects some molecular structures to a marked degree. At 448° I_2 is the correct formula, but at 1700° iodine must be written I. At 193° sulfur vapors are represented by S_8, but at 1719° by S_2. At 193° the G. M. V. (22.4 liters) of sulfur vapor (corrected to 0° and 760 mm.) weighs 256 g. This means the molecular weight at that temperature in 256. Since one sulfur atom weighs 32, there must be eight atoms in the molecule.

EXERCISE 6. — What must one liter of sulfur vapor weigh at 1719°?

EXERCISE 7. — The use of molecular formulas may seem puzzling at first, but it soon becomes a real convenience. The following example will show this: when limestone is heated to white heat in the kiln it forms quicklime and carbon dioxide:

$$CaCO_3 \rightarrow CaO + CO_2.$$

How many liters of carbon dioxide can be liberated from 25 g. of limestone? The answer is found at once. The formula $CaCO_3$ represents a definite quantity, the gram-molecular weight, or 100 grams. So does CO_2 represent one gram-molecular weight. But the molecular weight in grams of any gas occupies 22.4 liters. (See Gram Molecular Volume.) Now if 22.4 liters of carbon dioxide are released from 100 g. of limestone, 25 g. will release $\frac{25}{100} \times 22.4$ or 5.6 liters:

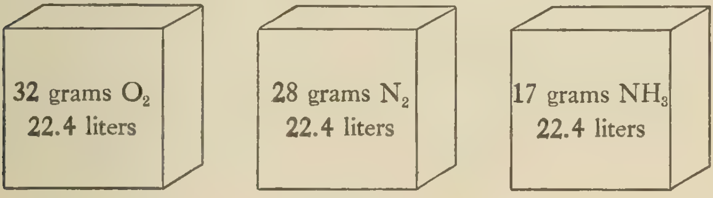


FIG. 30

$$\begin{array}{l} CaCO_3 \rightarrow CaO + CO_2 \\ 100\text{ g.} \rightarrow 56\text{ g.} + 44\text{ g. (or 22.4 l.)} \end{array}$$

EXERCISE 8. — How many liters of hydrogen are released by the action of 40 g. aluminum on sulfuric acid?

Exact Atomic Weights. — Before 1858 the distinction between atoms and molecules was not usually made. Avogadro himself saw it, but his famous hypothesis was not accepted until Cannizzaro emphasized the distinction and insisted on making Avogadro's law the foundation of all atomic weight calculations. This brought chemists to agreement on the present system of weights.

In 1905 an international committee of chemists decided to change the relative atomic weights from H=1 exactly and O=15.88 to O=16 exactly and H=1.008. The reason for the change was that oxygen unites directly with far more elements than does hydrogen, so fewer laboratory operations and fewer experimental errors are involved by making oxygen the center of the system.

Berzelius, early in the last century, made remarkably accurate determinations of atomic weights, but later Stas surpassed him and in recent years Morley and T. W. Richards have done the finest work of the sort on record. Berzelius used 100 as the atomic weight of oxygen.

There is always a greater experimental error in determining the density of a gaseous compound (and hence its molecular weight) than in determining the equivalent weight of an element. For example, suppose 22.4 liters of the volatile chloride of a new element "E" are found to weigh 116 g. This fact places the molecular weight at 116. By analysis of this chloride we learn that 40 per cent of it is "E" and 60 per cent of it chlorine, that is, they unite in the proportion 40: 60.

The weight of E equivalent to 35.46 g. of chlorine (atomic weight) is readily calculated from the proportion

$$60 : 40 = 35.46 : x \text{ (g. of E)}$$
$$x = 23.64 \text{ g.}$$

As stated on page 8 the atomic weight of an element is the same as the equivalent (or combining) weight or at most a small multiple of it. Thus we know that 23.64 or 47.28 or 70.92 etc. is the *exact* atomic weight of E. Since the molecular weight of this chloride has been found to be 116 (within the limit of experimental error) and 40 per cent of this weight is due to E, it is evident that 46.4 of the total molecular weight of 116 is due to E. This we shall call the weight of one atom unless later we find another compound in which the part of the molecular weight due to E is less than 46.4. At a glance we see that 46.4 is nearly but not quite 2×23.64. But for the greater experimental error in determining the molecular weight of the chloride this value would be exactly 2×23.64. Consequently we accept 47.28 as the exact atomic weight of E. To make the illustration clearer we purposely exaggerated the probable error in determining the weight of 22.4 liters of the volatile chloride.

Since the part of the molecular weight due to chlorine is about 69.6, there must be two atoms of chlorine in each molecule and the formula of the chloride must be ECl_2. The valence of E is 2.

Exercise 9. — Suppose 22.4 liters of a volatile bromide of a new element weigh 203 g. and 60 per cent of the compound is found, by analysis, to be the new element "E." What is the atomic weight of E, its valence and the formula of the compound?

To determine molecular weights of solids that do not volatilize readily or without decomposition we have recourse to a study of the freezing-point lowering of solutions, the boiling-point rise, and the osmotic pressure of solutions. All these methods will be discussed later.

Law of Dulong and Petit. — In 1818 Dulong and Petit observed that the product of the atomic weight of an element by its specific heat is equal to about 6.4. (The specific heat of a substance is the number of calories required to raise the temperature of one gram 1° C. The specific heat of water is the highest of all, 1.0, while that of copper is 0.1.) The law does not hold accurately but it is sufficient to settle many disputes, and invaluable in determining the atomic weight of an element which has no volatile compound.

$$\text{at. wt.} \times \text{sp. heat} = \text{product}$$
$$\text{Zn}, 65.4 \times 0.093 = 6.1$$
$$\text{Hg}, 200 \times 0.0335 = 6.7$$
$$\text{Cu}, 63.57 \times 0.0923 = 5.88$$
$$\text{Fe}, 55.5 \times 0.1098 = 6.12$$

Exercise 10. — It requires 2400 calories to raise the temperature of 4 kg. of an elementary substance 8°. What is its atomic weight?

Exercise 11. — Compare the relative amounts of heat required to raise a thousand atoms of zinc 1° and a thousand atoms of iron 1°. Disregard the slight difference in the product 6.1 and 6.12 in the above table.

Exercise 12. — Represent Gay-Lussac's law graphically for hydrogen chloride and ammonia, as was done for water on page 82. One volume of hydrogen reacts with one volume of chlorine to form two volumes of hydrogen chloride. Three volumes of hydrogen react with one volume of nitrogen to form two volumes of ammonia.

Exercise 13. — A certain compound contains, by analysis, 29.40 per cent of calcium (Ca), 23.56 per cent of sulfur (S), and 47.04 per cent of oxygen. The molecular weight is 136.2. Using these values and the table of atomic weights calculate the formula. See the discussion at the first of this chapter.

CHAPTER VIII

SOLUTIONS

A solid and a liquid may be so intimately mixed that separate particles of the solid are no longer seen. With certain reservations to be given later we may call this mixture a *solution.* Salt water is a good illustration. If the mixture is less intimate, so that minute particles of the solid may be seen with the microscope, we may call it a *suspension.* Two liquids may also mix so completely as to deserve the term *solution.* If less thoroughly mixed minute droplets of one liquid suspended in the other may be seen. Such a mixture is called an *emulsion.* Milk is an example.

A crystal of potassium permanganate half the size of a grain of wheat gives a perceptible pink color to every part of twenty liters of pure water. Each cubic centimeter contains about twenty drops, so in twenty liters, or twenty thousand cubic centimeters, there must be 400,000 drops. Each drop contains $\frac{1}{400,000}$ of the weight of the fragment of permanganate which weighed possibly 0.02 g. Nor is this the limit of such subdivision. Try the same experiment with a dye such as methylene blue or malachite green. Start with 0.01 g. in one liter. Pour 10 cc. of this into a liter flask and fill it with pure water. The concentration is now only $\frac{1}{100}$ that of the first solution. Take out 10 cc. of this second solution, dilute to a liter as before, and continue until the color is barely perceptible. Now calculate the weight of dye in a single drop.

Solutions never settle and are homogeneous to the eye. Suspensions or emulsions settle, sooner or later, and are not homogeneous under severe tests. In a true solution the particles of dissolved substance are single molecules or, at most, groups of a few molecules.

Types of Solution. — We are most familiar with solutions of solids in liquids, but liquids and gases may also be dispersed in liquids to form solutions. When a beaker of tap water is warmed bubbles of dissolved air may be obtained. Furthermore, solids dissolve in solids and liquids dissolve in solids. Some alloys are mixtures of metals so intimate as to deserve the name solution. A disk of gold was once clamped against a rod of solid lead and kept four years locked in a safe of the Bank of England. At the end of that time thin shavings of lead were cut off and analyzed. The gold had penetrated 7 mm. into the lead, forming a solid solution.

To stretch imagination still farther we may add that gases dissolve in solids. Palladium under certain conditions dissolves over eight hundred volumes of hydrogen.

Hardened steel is probably a homogeneous solid solution of carbon in iron (martensite) but softer steel is a mechanical mixture of pure iron and a carbide of iron.

Some substances dissolve quite simply; others first react with the solvent to form soluble compounds, which then dissolve.

EXERCISE 1. — To which type of solution does dilute sulfuric acid belong? Ordinary hydrochloric acid from the desk bottle? Ammonia water? Table syrup?

Definitions. — The liquid in which a solid or gas has been dispersed to form a solution is called the ***solvent*** and the substance dissolved the ***solute***. In the case of two liquids or two solids, each one may be said to be dissolved in the other, though the one present in larger quantity is usually termed the solvent.

By ***concentration*** we mean the amount of solute dissolved by a definite quantity of the solvent, often referred to as so many grams per 100 cc. of solvent (or even of solution). A solution containing relatively very little of the solute is *dilute*. In a *concentrated solution* there is a large amount of dissolved substance. Solutions may be made more concentrated (up to a certain limit) by adding more solute, preferably finely powdered, and shaking or stirring some time or by evaporating a dilute solution to remove part of the volatile solvent. Carried to the limit this is *evaporating to dryness* (in the case of solids in liquids) and the solute is recovered as a dry solid.

It is often incorrectly stated by the student that a saturated solution is one that contains all it can hold of the dissolved substance. That this is an error is readily proved by the formation of *supersaturated* solutions. Stir powdered sodium sulfate ($Na_2SO_4 . 10\,H_2O$) for some time in water at 30°, making sure that some is left over. Let settle and decant most of the solution into a clean flask, taking care that no fragment of the solid is transferred. Cover the flask to keep out dust and let cool. Now this solution, saturated at 30°, contained all it could hold, or it would have taken up more when it had the chance. After cooling to 15° the solution should throw down part of the solute because, in general, solids are less soluble on cooling. Yet this particular one continues to hold at 15° all it held at 30°. The same thing can be done with photographer's "hypo." We call the solution at 15° *supersaturated* and the natural definition — that it contains *more* than it can hold — is absurd. But toss in a minute fragment of a crystal of sodium sulfate and quickly a beautiful network of crystals radiate from the fragment. The amount thus crystallizing out is the difference between the amounts securely held at 30° and 15°. We now see a more accurate definition.

A *saturated solution* is in equilibrium with the undissolved substance. That is, when we stir sugar, for example, into water it continues to dissolve until the rate at which the sugar molecules in solution deposit on the lumps of solid sugar just equals the rate at which the solid throws molecules into the solution (Fig. 31). There is then no further change in the quantity in solution, but there is ceaseless activity. If a perfect crystal of alum with a cavity dug in the side be placed in a saturated solution of alum for several days, with no evaporation permitted, it is observed that the cavity fills up but the crystal weighs no more. The whole surface of the crystal has steadily dissolved and steadily been replaced, but in the accustomed regular form without cavities or broken edges.

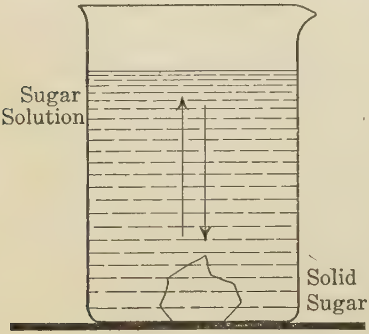


FIG. 31

A *supersaturated solution* is in unstable equilibrium and if placed in contact with some of the solid solute it throws down the excess over the amount held by a saturated solution.

EXERCISE 2. — If a clear solution of "hypo" ($Na_2S_2O_3$) were given you to test, how could you tell whether it was unsaturated, saturated, or supersaturated?

Measuring Solubility. — Water comes near being the "universal solvent" hunted for by the alchemists. Most so-called insoluble substances dissolve in water to a minute extent at least, as can be shown by electrical conductivity measurements. That glass dissolves noticeably is readily observed by adding powdered glass (greatly increased surface) to water containing a drop or so of the indicator, phenolphthalein. The purple color seen is characteristic of basic solutions. Glass and water react to form a small amount of a base. Even metals dissolve. Water in a copper vessel is slowly sterilized by the minute amount of copper thrown into solution. There are many degrees of solubility. Limestone ($CaCO_3$), called calcium carbonate in its pure form, dissolves to the extent of 0.00013 g. in 100 cc. of water, while 143 g. of potassium hydroxide dissolve in the same quantity of water.

The *temperature effect* on solubility must be considered in any of these quantitative statements. Nearly all solids are more soluble with rise in temperature, but there are a few exceptions, notably some calcium salts of organic acids. (Gases, however, are less soluble with rise in temperature.) Potassium nitrate is seven times as soluble at 70° as at 8°. There can be no accuracy, then, in a solubility statement unless the exact temperature of the measurement is given. This is usually 18° or 20°, the common working temperatures of our laboratories.

To make a solubility measurement we merely determine the number of grams of solute taken up by 100 cc. of water in a saturated solution at a definite temperature. This may be done by slowly stirring the powdered solid into water until no more is dissolved and keeping a record of the weights. There is much chance for error here, as some solids dissolve slowly. It is more accurate to stir in an excess and, after much stirring and settling, remove an accurately weighed or measured portion of the clear solution and carefully evaporate it to dryness on a steam bath. The loss in weight represents the water and the residue the solute. The results can be calculated as grams per 100 cc. of water (or 100 cc. of solution if preferred). Less time is required if one heats an excess of solid with water at a higher temperature than the one at which the measurement is to be made. The solution is then cooled and held a short time at the exact temperature desired until the excess has deposited and settled. A measured portion is then evaporated to dryness as before.

The solubilities at various temperatures may be plotted in the form of curves using the ordinates to represent the number of grams of anhydrous solid dissolved by 100 cc. of water. The abscissas represent temperatures.

With the curves on page 90 the solubility at any temperature may be read at a glance. What is the solubility at 18° and 90° of lead nitrate? Of sodium chloride at 77°?

Exercise 3. — Plot points on the solubility page according to the following approximate data and then connect these points in smooth curves (or straight lines, as the case may be). Label them neatly, using pencils.

	0°	10°	30°	50°	70°	90°	100°
Potassium Alum	6.5 g.	8.0 g.	17.5 g.	32.0 g.	113.0 g.		
Ammonium Chloride	29.0 g.	33.0 g.	42.0 g.	50.0 g.	60.0 g.	72.0 g.	78.0 g.

Temperature and Volume Changes of Solutions. — The student has already observed the astonishing amount of heat released when concentrated sulfuric acid is mixed with water and perhaps he may have dissolved anhydrous calcium chloride in water with a marked rise in temperature. The heat of solution in these cases probably involves an actual chemical reaction between solute and solvent. One gram molecular weight of concentrated sulfuric acid added to a large volume of water releases 39,170 cal. On the other hand one gram molecular weight of ammonium chloride *absorbs* 3,880 cal. on dissolving. Many salts produce this cooling effect or, in other words, their heat of solution is negative. This is very marked in the case of potassium iodide. This cooling effect may depend upon changes in the aggregation of water molecules caused by the dissolved substance.

As a rule the volume of a solution is less than the sum of the volumes of solute and solvent, but in the case of ammonium chloride and water it is greater. There are a few such exceptions. Gases dissolved in water may increase the volume. One liter of water saturated with ammonia gas increases to 1.580 liters at 14°.

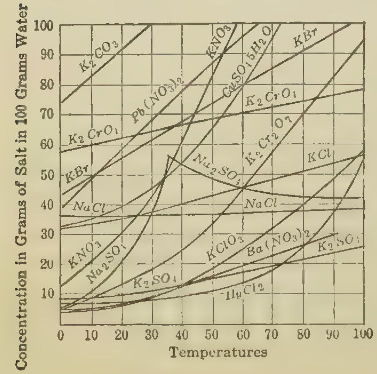


Fig. 32

Breaks in Solubility Curves. Transition Points. — Referring to Fig. 32, the chart of solubility curves, we observe a peculiar break, or sharp peak, in the curve for sodium sulfate. Using $Na_2SO_4 . 10 H_2O$ we find that its solubility increases up to 32.4° and then suddenly decreases. The fact is that at 32.4° this hydrate loses its water of crystallization:

$$Na_2SO_4 . 10\,H_2O \rightarrow Na_2SO_4 + 10\,H_2O.$$

Above 32.4° the curve represents the solubility of anhydrous sodium sulfate, Na_2SO_4, this salt being less soluble with rise in temperature. In other words this sharp point is the intersection of the two curves for these two crystalline forms of sodium sulfate. Such points, or temperatures, are called *transition points* and represent a distinct chemical change.

EXERCISE 4. — Look up the curve for calcium chloride and explain it.

EXERCISE 5. — If you were in a hurry to dissolve sodium chloride would you use hot or cold water?

EXERCISE 6. — Salt solutions are heavier than water. To dissolve commercial quantities of some solid substance without the expense of stirring or heating, would it be better to place the solid at the bottom of the vat or on a perforated shelf near the top?

Solubility of Liquids in Liquids. — Many pairs of liquids mix (dissolve in each other) in all proportions. Water and alcohol, water and sulfuric acid, water and glycerine are examples. But "oil and water" do not mix at all. It is true that an emulsion of minute droplets of oils in water can be made, but these droplets contain thousands of molecules and so are not in true solution. Other liquids dissolve in each other to a limited extent. If ether and water are shaken and allowed to stand an ether layer rises to the top with a water layer beneath. Analysis shows the presence of a little water dissolved in the ether layer and a little ether dissolved in the water layer. From these illustrations we see that liquids may be *completely miscible*, *partially miscible* or *immiscible*.

EXERCISE 7. — Give an illustration of each type.

Solubility of Gases in Liquids. Henry's Law. — In 1803 Henry observed that at any definite temperature *the solubility by weight of a gas in a liquid is proportional to the pressure* of the gas. At 0° and 760 mm. only 2 cc. of hydrogen dissolve in 100 cc. of water, but at two atmospheres (1520 mm.) twice this much, or 4 cc. of hydrogen as measured at one atmosphere, dissolves in 100 cc. of water. However, at the new pressure of 2 atmospheres the volume of hydrogen dissolved will be only 2 cc., weighing just the same. Ammonia (NH_3) at 0° and 760 mm.

dissolves to the extent of 114,800 cc. in 100 cc. of water, but its solubility does not follow Henry's law. In fact, all very soluble gases are exceptions, probably because they react to some extent with water. Certainly ammonia does, forming ammonium hydroxide (NH_4OH). Hydrogen chloride (HCl) is very soluble, while air is but slightly soluble.

With rise in temperature all gases are less soluble in liquids. Warming ammonia water drives off all the dissolved gas. Passing a stream of another gas, say air or steam, through a solution of a gas in water removes the dissolved gas for reasons given in the next paragraph.

Exercise 8. — What weight of ammonia dissolves in 1 l. of water at 0° and 760 mm.?

Exercise 9. — Would Henry's law hold closely for the solubility of hydrogen chloride in water? Of nitrogen?

Solubility of Mixed Gases. — If a liter of hydrogen and a liter of nitrogen at 760 mm. be forced together in a one-liter vessel, the total pressure becomes two atmospheres and each gas exerts its own part of the pressure (one atmosphere). If mixed in a two-liter vessel the hydrogen expanding to twice its previous volume could exert only one half of one atmosphere's pressure (Boyle's law). But the sum of this and a corresponding half atmosphere for nitrogen is one atmosphere for the two gases. Each attends to its own pressure as if the other gas was not present.

If a bottle of air be closed with a stopper containing a mercury pressure gauge or manometer, the pressure may be read in millimeters of mercury. Now if a thin bulb of water in the bottle be broken the release of water vapor inside the bottle adds to the air pressure, as shown by the rise of mercury in the manometer. Such experiments as these led Dalton in 1802 to state that *in a mixture of gases each gas exerts the same pressure as if it alone occupied the entire vessel and the total pressure is the sum of the partial pressures of the different gases.* Of course this law does not hold for gases that react.

The natural consequence of this fact is that in a mixture of gases over a liquid each one dissolves according to its own partial pressure (see Henry's law as well as Dalton's) independently of the presence and pressure of other gases. For example, air is a mixture of about four volumes of nitrogen and one of oxygen. At normal pressures (760 mm.) the oxygen is responsible for only 152 mm. of this pressure and nitrogen for the other four fifths or 608 mm. The oxygen of air dissolves in water to the exact extent that it would were the nitrogen not present. But if the nitrogen of our atmosphere suddenly ceased to exist, the oxygen remaining would exert a normal pressure of only 152 mm. and just as much of it would dissolve in rivers and lakes as at present. Oxygen at 760 mm. (five times its partial pressure in ordinary air) is five times as soluble as when found in air at 760 mm.

If a gas, not very soluble in water, is bubbled through ammonia water, for example, all the ammonia is removed because the stream of other gas (air, perhaps) sweeps the ammonia gas just above the liquid away and thus reduces its partial pressure in the air immediately above the liquid nearly to nothing at all. Since the solubility of ammonia depends on its pressure as a gas above the liquid, it is evident that it will under such conditions pass continuously out of the liquid. This is really a steady disturbance of solution equilibrium. Air and steam are both used to remove volatile substances from solution. In boiling ammonia water the escape of steam bubbles does much the same thing as if a stream of steam were led into the solution from outside.

EXERCISE 10. — How increase the solubility of carbon dioxide in water? How decrease it? Explain the effervescence of soda water.

Law of Partition. — In the chapter on the halogens some mention was made of the very slight solubility of iodine in water and its great solubility in carbon disulfide. A dilute solution of iodine in carbon disulfide has a beautiful violet color. At greater concentrations the solution is almost black. If we shake a small crystal of iodine in water until saturated, filter and then add carbon disulfide to the filtrate, with shaking, we observe a violet color in the heavy carbon disulfide layers. Most of the iodine has been *extracted* from the aqueous solution by the carbon disulfide, in which it is far more soluble. In fact the iodine is divided between the two solvents in the exact ratio of its solubility in the two. If it is one hundred times as soluble in carbon disulfide as in water, only one part will remain in the water and one hundred parts in the carbon disulfide. The dissolved iodine is in constant motion, passing from one liquid to the other, as indicated by the following equilibrium:

$$I_2 \text{ (in water)} \leftrightarrows I_2 \text{ (in carbon disulfide)}.$$

This equilibrium can be disturbed by adding something that reacts with the iodine in the water layer. Sodium thiosulfate ("hypo") or even chlorine water (because of its hypochlorous acid) will do this. As fast as the very small amount of iodine left in the water is used up, more replaces it from the carbon disulfide, and finally, after sufficient additions, with shaking, all the iodine is removed from the carbon disulfide, as shown by the complete loss of violet color.

Exercise 11. — What is the reaction between chlorine water and iodine? Delay this answer until the halogens have been studied.

The system ether-water can be treated with iodine in the same way. Removal of part of a dissolved substance by addition of a second solvent is called ***extraction.*** Ether is often used for this purpose, as it is a splendid solvent for many substances. Animal and vegetable materials yield extracts in such solvents. Melted zinc extracts silver from melted lead in Parke's process. Of course the law of partition (which has a relation to Dalton's law) applies to immiscible solvents.

Exercise 12. — 100 g. of the substance x, twice as soluble in benzene as in water, is dissolved in 1000 cc. of water. 1000 cc. of benzene are added and shaken in order to extract the substance x. How many grams are removed from the water? If instead of using 1000 cc. of benzene at one time only 500 cc. be used, how many grams are removed? Now if a second 500 cc. be added to the water which has just been treated, how many grams are removed? In extractions is it better to use all the solvent at one time or in fractions?

Molar and Normal Solutions. — *A molar solution contains a molecular weight in grams of solute in a liter of solution.* Since the molecular weight of sulfuric acid is 98, a molar solution of this acid contains 98 g. per liter. Note that we did not refer to 1000 cc. of solvent, but 1000 cc. of solution, a very different thing. A molar solution of sodium chloride contains 58.45 g. per liter of solution.

Exercise 13. — How make 500 cc. of molar copper sulfate? Remember that the "blue vitriol" used is $CuSO_4.5\ H_2O$.

Exercise 14. — How make half molar potassium nitrate?

Another method of referring to concentrations is the system of normal solutions, of great convenience in analysis.[1] *A normal solution contains* 1.008 *g. of combined hydrogen, or its equivalent, in one liter.* The molecular weight of hydrogen chloride is 36.468, and of this 1.008 is the part due to hydrogen. Therefore 36.45 g. of hydrogen chloride in a liter of solution constitutes normal hydrochloric acid. This happens to be molar hydrochloric acid also, but molar and normal solutions are not always the same.

A normal solution of sodium hydroxide (NaOH) contains 40 g. per liter, because 40 g. of sodium hydroxide are equivalent to 1.008 g. of combined hydrogen. The following equation shows why this is so:

$$\mathrm{Na}\,\boxed{\mathrm{OH+H}}\,\mathrm{Cl} \rightarrow \mathrm{H_2O+NaCl}.$$

$$40.008\ \mathrm{g.}\quad 36.468\ \mathrm{g.}$$

In sulfuric acid a molecular weight in grams (98 g.) per liter (molar solution) contains 2.016 g. of combined hydrogen and is therefore twice normal, 2 N. To make normal sulfuric acid 49 g. per liter of solution is sufficient.

A normal solution of a salt contains one gram equivalent of the metal per liter of solution. 23 g. of sodium are equivalent to 1.008 g. of hydrogen, so a normal solution of sodium chloride contains 58.45 g. of the salt per liter because 58.45, the molecular weight of sodium chloride, is made up of 23 for sodium and 35.45 for chlorine.

The symbol for normal is N. Twice normal is 2 N and tenth normal 0.1 N or N/10.

EXERCISE 15. — How make a normal solution of hydrobromic acid (HBr)? Of potassium hydroxide? Of barium hydroxide, $Ba(OH)_2$?

EXERCISE 16. — How many grams of $Na_2SO_4 . 10\,H_2O$ in 800 cc. of N/5 solution? Of Na_2SO_4 in 800 cc. of N/5 solution?

EXERCISE 17. — Define equivalent weights.

Freezing Point Lowering. — That salt water freezes at a lower temperature than pure water has long been known. Cavendish's secretary, Blagden, observed that the amount of this lowering of the freezing point was proportional to the concentrations of dissolved substance. For example, if 10 g. of glycerine in 1000 cc. of water froze a fraction of a degree below zero, then 20 g. of glycerine per 1000 cc. of water froze twice as far below zero and a 50 g. solution five times as far below zero. A most interesting point is brought out if gram-molecular weights of such substances as alcohol, glycerine, sugar and acetone, in 1000 cc. of water are frozen. They all freeze at about $-1.86°$. Hence the molar depression of the freezing point of water is 1.86°. We can obtain the molecular weight of a soluble substance by noting how many grams of it must be dissolved in 1000 cc. of water to lower the freezing point to $-1.86°$. If 80 g. are required, 80 is, of course, the molecular weight. If in another instance a solution froze at $-0.186°$ the lowering was only one tenth that produced by a molar weight, and hence the weight of solute used per 1000 cc. of water was only one tenth the molecular weight.

---

[1] This definition refers to acids, bases and salts, yet it does not hold for such acids as acetic. Only part of the hydrogen of acetic acid is really acidic, replaceable by a metal, and it is to this type of hydrogen that the definition refers.

46 g. of ethyl alcohol (C_2H_5OH) in 1000 cc. of water freezes at $-1.86°$ as does 342 g. of cane sugar ($C_{12}H_{22}O_{11}$) and 32 g. of methyl alcohol (CH_3OH). These are all gram-molecular weights. An important exception to these statements must be made for acids, bases and salts. They will be discussed later.

Common salt and ice in right proportions make a freezing mixture used in ordinary ice-cream freezers because the salt lowers the freezing point of water to $-21°$ C.

Exercise 18. — If a solution made by dissolving 8 g. of a substance in 1000 cc. of water freezes at $-0.4°$, what is the molecular weight of the substance?

The molecular depression of the freezing point of benzene is 4.9° and of phenol 7.6°. Of course we refer this to 1000 g. of solvent as, indeed, is also true for water.

Exercise 19. — How much should 6.5 g. of naphthalene ($C_{10}H_8$) in 125 g. of benzene lower the freezing point?

Boiling Point Rise. — The work of Raoult on freezing point lowering was applied (1882) to a study of the effect of dissolved substances on vapor pressure. Since a solute interferes with the evaporation of a solvent by lowering the vapor pressure of the solvent, the solution must be made hotter to produce a vapor pressure just equal to the pressure of the atmosphere, that is to make the liquid boil at 760 mm. Water boils at 100°, but Raoult found that if a molecular weight in grams of any substance (except acids, bases and salts) be dissolved in 1000 cc. of water the solution boils at 100.52°. The boiling point rise is 0.52°. In other words it requires more energy in the form of heat, to separate water from a solution than from pure water by evaporation. Obviously the molecular weight of such a substance as glycerine or sugar may be obtained by measuring the boiling point of any convenient solution and from this calculating how many grams of solute would be required to raise the boiling point 0.52°. To sum it up, the lowering of the vapor pressure of a solvent (and the consequent rise in boiling point) caused by dissolved substances other than acids, bases and salts, is directly proportional to the molecular concentration of the solute. The boiling point rise caused by one formula weight in grams of solute per 1000 grams of solvent is 0.52° for water, 1.67° for acetone and 2.67° for benzene. Raoult's law does not hold where there is reaction between solute and solvent or where there is much "association" of solvent molecules into groups.

Exercise 20. — What should be the boiling point of a solution containing 150 g. of cane sugar ($C_{12}H_{22}O_{11}$) in 800 cc. of water?

Exercise 21. — A solution of 45 g. of the substance AB in 1000 g. of benzene freezes at $-1.2°$. What is the molecular weight of AB?

Osmotic Pressure. — We have seen that a crystal of some substance such as copper sulfate placed at the bottom of a tall cylinder of water slowly dissolves and diffuses against gravity into every part of the liquid. There is actually a pressure of diffusion called osmotic pressure which can be measured by separating the solution from pure water by a membrane permitting the free passage of water but not of the dissolved substance. Such membranes are called "semi-permeable" but none are quite perfect in their action. In Fig. 33 we

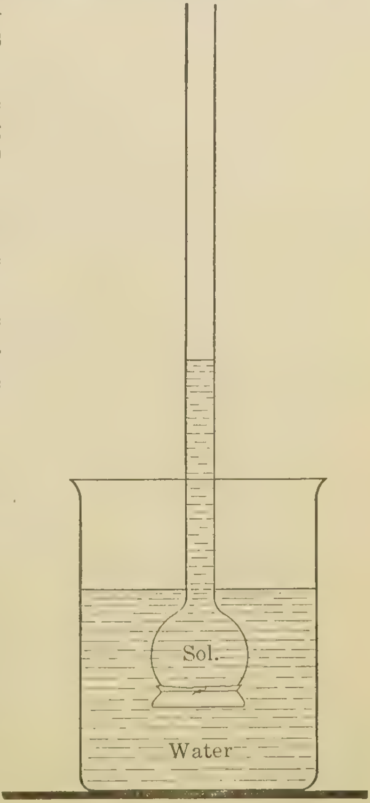


Fig. 33

represent a simple device for demonstrating osmotic pressure which is, however, too crude for accurate quantitative study. A sheet of wet parchment paper is tied over the end of a thistle tube and the tube partly filled with a concentrated sugar solution containing a little coloring material such as cochineal. The tube is firmly fixed in an inverted position in a beaker of pure water. After a few hours the level of the liquid in the narrow stem (marked with a label) has risen to a considerable height — to such a height that the weight of the column of liquid just equals the osmotic pressure of the solution. If a narrow-stemmed funnel is not at hand, a coarse capillary tube can be connected to the cup of the thistle. The rate of entrance of liquid into the bulb is thus magnified to the eye.

The pure water passes through the membrane (slowly) in both directions, but passes into the solution faster than it passes out. The result is an increase in the volume of liquid in the bulb shown by a rise in the narrow tube. The pressure set up is measured by the weight of the column of solution.

The flow of liquid is called *osmosis*. Another method of measurement is to note the exact amount of pressure applied to the solution that just prevents flow of water through the membrane.

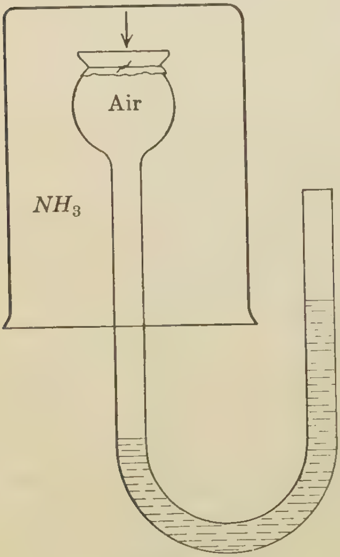


FIG. 34

A parallel experiment with gases helps to make clear our conceptions of osmotic pressure. A large thistle tube (or its equivalent) is bent as in Fig. 34 and after filling the bend with some oil (water will not do and mercury is too heavy to show the pressure clearly) the top is tightly closed with thin muslin thoroughly wet with water. This film of water is a membrane permeable to ammonia gas but only slightly permeable to air. A large beaker filled with ammonia gas is inverted over the thistle tube, and, if necessary, a stream of the gas led into the beaker from a generator. Ammonia dissolves in the film of water and escapes into the air space within the bulb. A bit of wet red litmus paper in the bulb turns blue. Since the air does not dissolve noticeably in the water the flow of gas is all one way except that the ammonia on reaching the interior of the bulb naturally diffuses out. Soon the pressure of ammonia on both sides of the membrane will be the same, in this experiment one atmosphere. But the air within the bulb was put there under one atmosphere so the total pressure within the bulb becomes two atmospheres — one due to air and one to ammonia. This pressure is shown by rise of oil in the outer arm of the bent tube or manometer. When equilibrium is reached the pressure on the wet-muslin membrane is actually due to the pressure exerted by the air within the bulb. In actual practice the weak water film breaks and the full theoretical pressure is not attained.

This latter experiment may be compared with the one using sugar solutions and water on opposite sides of a parchment paper membrane. In the second case water on both sides moves freely through and comes to equilibrium when the pressure due to water alone is the same on both sides. The additional pressure on the membrane due to sugar molecules is what we measure as osmotic pressure. However, we measure directly the pressure with which water tends to flow in. In the first case the air enclosed in the bulb is comparable to the sugar and the ammonia present on both sides of the water film after equilibrium is comparable to the water in the other experiment. There are different theories as to the cause of osmotic pressure, but the above is a very good working conception of the phenomenon.

Using solutions against solvent we find the *osmotic pressure is proportional to the concentration of the solute in the solution.* That is, a 10 per cent sugar solution has twice the osmotic pressure of a 5 per cent solution. If a more dilute solution is placed on one side and a more concentrated on the other, the pressure will be proportional to the difference in concentration. Water (or other solvent) always tends to dilute the solution of greater concentration. This tendency can be checked, as was mentioned before, by applying an equal and opposite pressure.

The osmotic pressure is directly proportional to the absolute temperature. This is really Charles's law for gases. Another fact of importance is that *at the same temperature equal numbers of molecules of different solutes in equal volumes of the solvent exert the same osmotic pressures.* It makes no difference whether large sugar molecules (342) or molecules one tenth their weight are compared. Mere *number of dissolved particles* per 1000 cc. solvent is all that counts. Furthermore, *the osmotic pressure of a dissolved substance* *is equal to the pressure it would exert if it were a gas occupying the same volume as that of the solvent.* Suppose that a gas of molecular weight 64 were quite soluble in water. This weight in grams (64 g.) occupying 22.4 liters (the G. M.V.) at 0° exerts one atmosphere pressure as a gas. If the same 64 g. of the gas be dissolved in 22.4 liters of water, its osmotic pressure equals one atmosphere.

A spectacular experiment illustrating osmotic pressure as well as the formation of semipermeable membranes is easily performed. Crystals of salts of nickel, cobalt, copper, lead, manganese and iron may be dropped into ordinary commercial water glass diluted with an equal volume of water. Small compact lumps of ferric chloride are excellent for the purpose. Water glass is sodium silicate and the fragment of nickel sulfate, for example, dissolving in the water of this solution reacts to form nickel silicate, a gelatinous material. This forms a sack, semipermeable in that it allows water to pass through in both directions but does not permit the molecules of nickel sulfate inside the sack to diffuse out. The concentration of the solution inside each little sack is greater than that outside because the fragment of crystal keeps it saturated. The result is shown by swelling and bursting of the sack. This lets out the contents, nickel sulfate, to react and form a new sack wall. Thus a tree-like growth upward (because of the lesser hydrostatic pressure above) appears with a startling rapidity in the case of ferric chloride and is quite appreciable in all cases. The "submarine forest" in many colors is worth observing for a day or so. The bursting of the sacks is a result of osmotic pressure of a more concentrated solution.

The most accurate measurements of osmotic pressure were made by Morse, Frazer and Holland at the Johns Hopkins University and by the Earl of Berkeley in England. Morse, in his classic research, used copper ferrocyanide supported by a clay wall as the membrane. Finely ground and sifted clays were pressed wet into a solid rod which was drilled into the form of a cup and then baked. This was filled with copper sulfate solution and set in a larger vessel of potassium ferrocyanide solution. The two solutions, aided in diffusion by an electric current, met inside the wall and formed a red precipitate of copper ferrocyanide. A mercury manometer was carefully attached to the cleaned cell or cup after filling with sugar solution (Fig. 35). It was then filled with the solution whose osmotic pressure was to be measured and placed in pure water in a bath whose temperature was carefully regulated. After equilibrium was reached the pressure was read. Many difficult precautions had to be taken, but pressures of many atmospheres were accurately measured. Frazer and Myrick (1916) have used delicate electric resistance methods for measuring very high pressures and reported accurate measurements of 270 atmospheres.

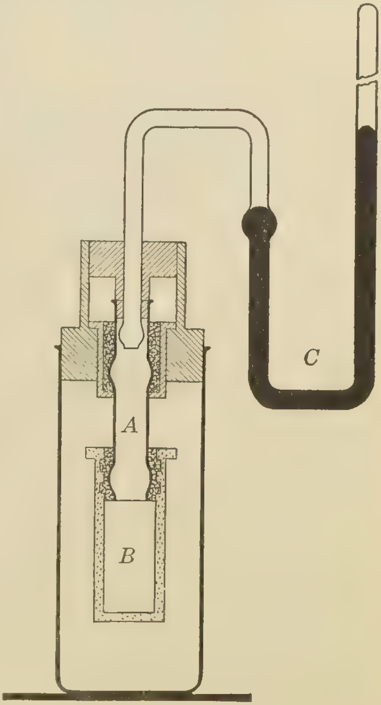


Fig. 35

Withered flowers revive in pure water because the water passes through the tissues of the flower, good semipermeable membranes, tending to dilute the concentrated juices of the plant. This dilution distends the flower. The rise of sap to great heights on a tree is said to be due to osmotic pressure. Osmosis is important in both animal and plant tissues. However, it is safer not to ascribe these phenomena solely to osmotic pressure. Plant and animal tissue combine chemically with water, becoming hydrated, as we say, and are in turn dehydrated by salts, sugar, etc. The biological side of the subject is complicated.

The osmotic pressure laws do not hold for acids, bases and salts for very good reasons soon to be developed.

Kinetic Molecular View of Osmotic Pressure. — Van't Hoff concluded that *substances in solution behave as if they were gases confined to the volume of the pure solvent.* Thus osmotic pressure is really quite similar to gas pressure and the laws of Boyle and Charles hold both for gases and for solutions (with certain exceptions).

EXERCISE 22. — Review the topics referring to vapor tension, deliquescence, and equilibrium. Now predict what must happen under the conditions represented in Fig. 36. Under the bell jar are two beakers; one containing a water solution (of sugar, for example) and the other pure water.

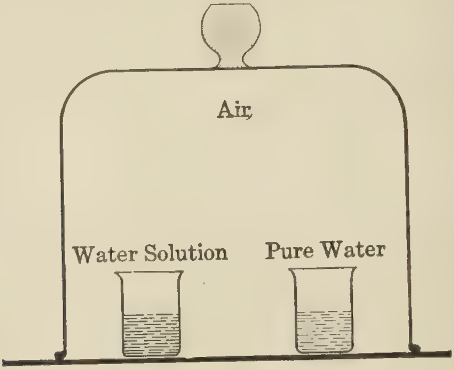


FIG. 36

CHAPTER IX

CHLORINE AND HYDROGEN CHLORIDE

CHLORINE

History. — Chlorine was first prepared by Scheele in 1774 by the action of manganese dioxide on hydrochloric acid. However it was thought to be a compound of hydrochloric acid and oxygen, even by Lavoisier. In 1810 Sir Humphry Davy tried in vain to reduce the supposed oxide and finally convinced the scientific world that this substance was really an element. He named it chlorine, from the Greek for "greenish-yellow."

Exercise 1. — In what connection have we heard of Scheele before?

Occurrence. — Chlorine is not found free in nature because it reacts so readily with many other substances, particularly metals. Its commonest compound is sodium chloride, common salt. This is found in sea water to the extent of nearly 3 per cent. Great Salt Lake contains 23 per cent. In some parts of the world salt is mined, and deposits are common. Magnesium chloride generally occurs with common salt. In fact the "wetting" of table salt and consequent refusal to go through the top of shakers is due to the deliquescence of the magnesium chloride impurity. Potassium chloride is found in a large deposit at Stassfurt, Germany, associated with sodium chloride and magnesium chloride. Silver chloride, "horn silver," is one of the ores of silver.

Preparation. — A few chlorides of the less active metals yield part or all of their chlorine on heating, but this is negligible as a source of chlorine:

$$PtCl_4 \rightarrow Pt + 2\,Cl_2,$$
$$2\,CuCl_2 \rightarrow 2\,CuCl + Cl_2.$$

The most convenient laboratory methods of preparation depend upon the oxidation of hydrogen chloride into water and free chlorine:

$$\boxed{O + 2\,H}Cl \rightarrow H_2O + Cl_2.$$

Oxygen alone does this only with extreme slowness unless aided by a catalyst at a favorable temperature (see the Deacon process), but good oxidizing agents such as potassium permanganate, manganese dioxide, sodium dichromate and lead dioxide will oxidize it rapidly without a catalyst. A concentrated solution of hydrogen chloride in water (called hydrochloric acid) is warmed (Fig. 37) with the oxidizing agent:

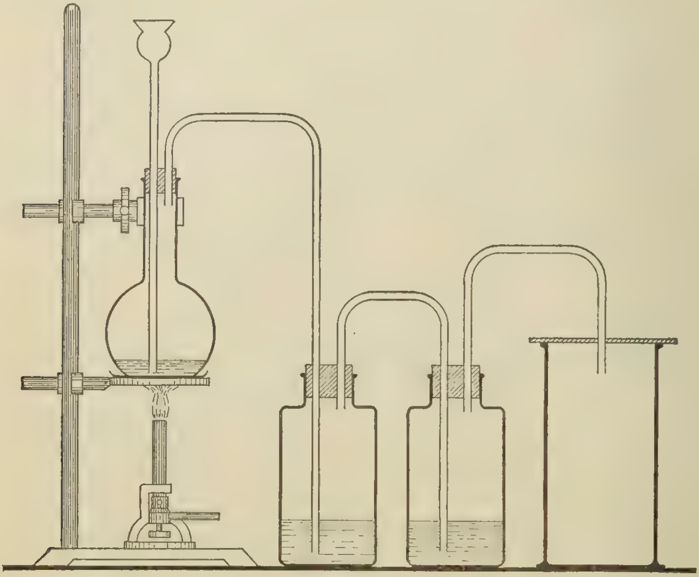


Fig. 37

$$MnO_2+4\ HCl \rightarrow 2\ H_2O+MnCl_4,$$
$$MnCl_4 \rightarrow MnCl_2+Cl_2.$$

The manganese tetrachloride, $MnCl_4$, is an oily liquid unstable unless kept chilled so it breaks down into the ordinary manganous chloride and free chlorine. Had we used manganous oxide, MnO, no chlorine would have been released:

$$MnO+2\ HCl \rightarrow H_2O+MnCl_2.$$

We may say that MnO_2 is an oxidizing agent and MnO is not, but this is only part of the truth. In MnO_2 the valence of the metal is four, and in its product, $MnCl_2$, the valence has dropped to two.

This fact introduced an extension of the idea of oxidation and reduction. A drop in valence of the positive element or radical in a compound is reduction. The MnO_2 was *reduced* by the HCl (which also means that the MnO_2 oxidized the HCl) because the manganese dropped in valence from four to two. In the reaction with MnO the valence of manganese was two and remained two in the product, $MnCl_2$.

EXERCISE 2. — The reactions of hydrochloric acid with lead dioxide, PbO_2, and lead monoxide, PbO, are similar to the above. Write the equations. Remember that the hydrogen of the acid unites with the oxygen of metallic oxides to form water.

In practice we generate the hydrochloric acid from the action of moderately diluted sulfuric acid on sodium chloride and oxidize it with manganese dioxide in the same operation (Fig. 36). The gas is passed through a little water to remove hydrogen chloride and through concentrated sulfuric acid to dry it. It displaces air from the receiving cylinder.

$$\begin{array}{ll}(1) & 2\,NaCl + 2\,H_2SO_4 \rightarrow 2\,NaHSO_4 + 2\,HCl \\ (2) & 4\,HCl + MnO_2 \rightarrow 2\,H_2O + MnCl_2 + Cl_2 \\ (3) & MnCl_2 + H_2SO_4 \rightarrow MnSO_4 + 2\,HCl \\ \hline \end{array}$$

$$(4)\quad 2\,NaCl + 3\,H_2SO_4 + MnO_2 \rightarrow 2\,NaHSO_4 + 2\,H_2O + MnSO_4 + Cl_2$$

Equations (1), (2) and (3) represent the *steps* in the complete reaction summed up in (4). In fact (2) is itself a summary of two reactions given earlier in this chapter. It is an excellent drill to work out such an equation as (4). Equation (1) was doubled to furnish 2 HCl for (2). Equation (3) furnishes 2 HCl also. Note that in balancing (2) we tried *at least one molecule* of MnO_2. This required four hydrogen atoms to take care of the two oxygen atoms in MnO_2, forming $2\,H_2O$. Also the one atom of manganese required four chlorine atoms to form $MnCl_4$ (which at once broke down into $MnCl_2+Cl_2$). Therefore 4 HCl was needed to satisfy these requirements for hydrogen and chlorine. In attempting to add (1), (2) and (3) to get (4) we must write on the left all the reacting substances originally mixed and on the right the final products. The intermediate substances are not included in a summary (HCl and $MnCl_2$ in this instance). Such a summary is difficult to remember and it is not best to attempt it. It may be worked out at any time by a logical development of the easily remembered steps. Potassium permanganate is an excellent but expensive oxidizing agent for the purpose of making chlorine. Concentrated hydrochloric acid diluted with about one third its volume of water is dropped slowly on the solid from a dropping funnel. The chlorine is released instantly without warming, and its flow ceases on stopping the addition of acid:

$$2\ KMnO_4 + 16\ HCl \rightarrow 8\ H_2O + 2\ KCl + MnCl_2 + 5\ Cl_2.$$

Potassium permanganate, being soluble in water, is in better contact with the acid than is the insoluble manganese dioxide. Sodium dichromate is also efficient in oxidizing concentrated hydrochloric acid:

$$Na_2Cr_2O_7 + 14\ HCl \rightarrow 2\ NaCl + 2\ CrCl_3 + 7\ H_2O + 2\ Cl_2$$

Compare this equation with the one for potassium permanganate. In each case enough hydrogen atoms from HCl molecules must be taken to unite with all the oxygen atoms of the oxidizing agent. Also, each metallic atom unites with enough chlorine atoms to form its stable chloride. Hence in the two equations the formation of KCl, $MnCl_2$, NaCl and $CrCl_3$. Any chlorine not needed by the metals escapes as gas.

EXERCISE 3. — How many liters of chlorine are released by the action of 45 g. potassium permanganate on an equivalent amount of hydrochloric acid?

Commercial Methods of Preparation. — Deacon's process was for a long time the leading method in Europe for the preparation of chlorine, but has never been used in the United States. Hydrogen chloride mixed with air is passed through a tube heated to 370°–400° and filled with porous stone (pumice) which has been soaked with a solution of cupric chloride or sulfate and dried. The pumice stone is merely a mechanical support for the catalyst, cupric chloride. It is probable that the cupric chloride ($CuCl_2$) releases chlorine on heating, and the resulting cuprous chloride (CuCl) forms copper oxide (CuO) with the air. Hydrogen chloride reconverts the oxide into cupric chloride and so on. However the catalyst may function, the general effect is oxidation of hydrogen chloride:

$$4\ HCl + O_2 \leftrightarrows 2\ H_2O + 2\ Cl_2.$$

It is a reversible reaction, and since all four substances are gases in good contact it is impossible to oxidize 100 per cent of the hydrogen chloride. Equilibrium is reached when 80 per cent of the hydrogen chloride has been converted into chlorine. Naturally the chlorine is contaminated by the steam, the 20 per cent unused hydrogen chloride, and all the nitrogen of the air used, but it is suitable for use in chlorinating lime to make bleaching powder.

Exercise 4. — How many cubic meters of *air* will be required to oxidize 10 kg. of hydrogen chloride?

Chlorine by Electrolysis. — The leading commercial method of making chlorine is by the electrolysis of water solutions of sodium chloride. Chlorine is evolved at the anode, which must be made of carbon, usually in the form of graphite, because the gas is so active it would react with metal anodes. At the cathode, usually iron, sodium is released, but of course it reacts at once with water to form sodium hydroxide and hydrogen. The sodium hydroxide is a valuable by-product. Since chlorine in the presence of water reacts with sodium hydroxide, it is necessary to keep the solutions around the two electrodes from mixing. Industrial chemistries will give the details. Most cells keep the liquids separated by a membrane of porous baked clay or asbestos. The electric current can be carried through such membranes, and solutions slowly pass through, but there is no great amount of mixing. The most modern device is to arrange a slow flow of liquid through the anode compartment into the cathode compartment. At the Edgewood arsenal near Baltimore the United States government used thousands of electrolytic cells to make the chlorine needed for poison gas manufacture in the Great War. The final production rate was 100 tons of chlorine every 24 hours. This was the largest chlorine plant ever built, but of course there is no demand in times of peace for such great quantities of the gas.

Molten sodium chloride conducts electricity and can thus be decomposed into chlorine and sodium. With no water present the sodium accumulates. This is the commercial source of metallic sodium.

Physical Properties. — Chlorine is a greenish-yellow gas 2.49 times as heavy as air. One liter weighs 3.220 g. at 20°. 100 volumes of water dissolves 226 volumes of chlorine. It can be liquefied at

18° by 16.5 atmospheres' pressure and its critical temperature is 146°. The liquid boils at −33.6° and freezes at −102°. The gas is very irritating to smell and fatal in any considerable quantities. When collected over water there is some loss because it dissolves in and reacts with water. It is less soluble, however, in water saturated with common salt. Since it attacks mercury it may not be collected over that liquid. Usually it is led into the bottom of any vessel filled with air and, being 2.49 times as heavy, displaces the air upward. Water saturated with chlorine at 0° deposits crystals of $Cl_2.8\,H_2O$. These have a very high vapor tension, decomposing readily on warming slightly. Faraday in 1823 used this property to liquefy chlorine, the first time this was achieved. Now every gas has been liquefied.

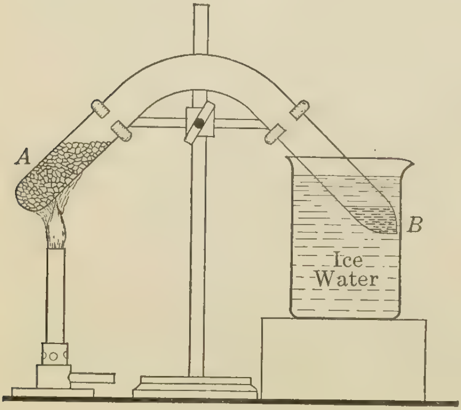


FIG. 38

Faraday sealed some crystals of the chlorine hydrate in a strong U-tube, warmed the end containing the crystals, and chilled the other end by ice and salt (Fig. 38). In the closed tube the pressure of the liberated chlorine became great enough with the aid of low temperature to liquefy the gas. The molecules were forced together by pressure and their motion lessened by cooling.

Chemical Properties. — Chlorine is one of the most active elements, more active than oxygen. It unites with nearly all the elements to form *chlorides.*

1. Action on Elements. — The metals, with but few exceptions, unite with chlorine. A piece of sodium in a bottle of *dry* chlorine gradually becomes sodium chloride, but if the sodium is first heated it burns brilliantly in the chlorine. So does calcium, forming calcium chloride. Thin copper foil, if heated, bursts into flame in a jar of chlorine. Even platinum is attacked by the gas. Most of the non-metals are attacked. Sulfur burns in chlorine to form sulfur chloride, used in the manufacture of mustard gas during the Great War. Antimony and arsenic, if powdered, unite with chlorine with a flash of flame.

Yet if chlorine be dried over phosphorous pentoxide it does not attack copper, etc. A trace of water is necessary as a catalyst.

Phosphorus unites with chlorine, burns in it in fact, to form a colorless liquid (PCl_3), phosphorous trichloride, and with an excess of chlorine this becomes PCl_5, phosphorous pentachloride, a yellow solid.

Chlorine and hydrogen unite very slowly in the dark, rapidly in diffused light and explosively in bright sunlight or the light of burning magnesium. Hydrogen chloride is formed. If a jet of burning hydrogen be lowered into a bottle of chlorine, it continues to burn with evolution of light and heat and formation of hydrogen chloride (Fig. 39). Direct union of the two gases is being used to some extent now to form pure "synthetic hydrochloric acid." There is, therefore, such a thing as combustion without oxygen:

$$H_2+Cl_2 \rightarrow 2\ HCl.$$

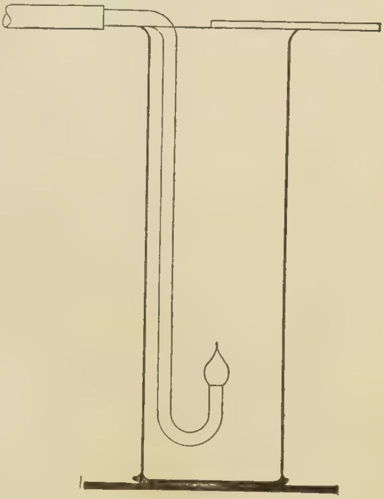


FIG. 39

2. ***Action on Compounds.*** — Chlorine will pull the hydrogen out of compounds and form hydrogen chloride. Natural gas (largely CH_4, methane) will burn in chlorine just as well as does hydrogen, but the flame is smoky, due to the liberated carbon:

$$CH_4+2\ Cl_2 \rightarrow C+4\ HCl.$$

A burning candle lowered into a jar of chlorine burns with a smoky flame. A paper wet with warm turpentine bursts into smoky flame in chlorine. The reaction is similar:

$$C_{10}H_{16}+8\ Cl_2 \rightarrow 10\ C+16\ HCl.$$

EXERCISE 5. — How many liters of hydrogen chloride at 0° and 760 mm. can be formed by the action of chlorine on 500 g. turpentine? Solve two ways.

Chlorine displaces some elements from compounds:

$$2\ KI + Cl_2 \rightarrow 2\ KCl + I_2,$$
$$2\ NaBr + Cl_2 \rightarrow 2\ NaCl + Br_2.$$

Here iodine and bromine are displaced. Chlorine is a more active element than either. With carbon monoxide it unites, in sunlight, to form phosgene, one of the greatest of poison war gases:

$$CO + Cl_2 \rightarrow COCl_2.$$

The carbon monoxide was readily made by reducing carbon dioxide with hot carbon.

Chlorine not only dissolves in cold water but reacts with it:

$$Cl_2 + H_2O \leftrightarrows HCl + HClO.$$

This is a reversible reaction, but the hypochlorous acid ($HClO$) slowly decomposes into hydrochloric acid and oxygen. Since this decomposition is accelerated by sunlight, chlorine water is best kept in dark bottles. Finally the equilibrium is displaced completely to the right and there is no longer any dissolved chlorine left, merely a solution of hydrochloric acid. The equilibrium is disturbed to the right rapidly if there is some reducing agent present to take up the oxygen from the hypochlorous acid. In other words the instability of hypochlorous acid makes it a good oxidizing agent.

We referred previously to the burning of a jet of methane (CH_4) in chlorine. In the sunlight the two gases react slowly as follows:

$$(1)\quad CH_4 + 3\ Cl_2 \rightarrow CHCl_3 + 3\ HCl$$
$$(2)\quad CH_4 + 4\ Cl_2 \rightarrow CCl_4 + 4\ HCl$$

$CHCl_3$ is chloroform and CCl_4 is carbon tetrachloride. This kind of displacement is sometimes called substitution. The hydrogen displaced is not set free but unites with part of the chlorine.

Types of Chemical Reaction.—

I. Combination. Two substances unite to form one substance. Example: $C + O_2 \rightarrow CO_2$.

II. Decomposition. One substance decomposes into two more. Example: $2\ HgO \rightarrow 2\ Hg + O_2$.

III. Double Decomposition. Two substances react to form two other substances. Example: $AgNO_3 + NaCl \rightarrow NaNO_3 + AgCl$.

IV. Displacement. One element displaces another from a compound. Example: $Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4$.

V. Substitution. One element displaces another which is not set free but escapes in combination with part of the displacing element. Example: $CH_4 + 3\ Cl_2 \rightarrow CHCl_3 + 3\ HCl$.

Exercise 6. — Write three examples of each type.

Uses of Chlorine. — Chlorine finds its greatest use as a bleaching agent. Colored strips of calico, red geraniums, etc., hung in bottles of chlorine soon lose their color. If, however, the gas and the colored object are thoroughly dried, no bleaching takes place. The water is necessary as a catalyst.

The effect of water is easily understood from the equation just given:

$$Cl_2 + H_2O \leftrightarrows HCl + HClO.$$

The hypochlorous acid oxidizes colored substances into colorless ones so the chlorine bleaches indirectly. Printers' ink cannot be bleached because its color is due to carbon, on which hypochlorous acid has no effect. Chlorine is too destructive to be used on silk, feathers and the more delicate materials. Even cotton is slightly weakened, so the chlorine must be thoroughly washed out. Great quantities of the gas are passed over lime to form bleaching powder, from which chlorine can be released as needed.

As a disinfectant it is invaluable. Many great cities add a little chlorine to their water supplies to kill bacteria, which it does most efficiently and cheaply. Typhoid epidemics are quickly checked by its use.

Gold is extracted from its ores by the action of chlorine in forming soluble gold chloride. This is only one of the processes used.

It is possible to chlorinate natural gas which contains methane (CH_4) to form chloroform ($CHCl_3$) and carbon tetrachloride (CCl_4) and this will doubtless be done soon on a large scale. Many useful organic compounds are formed in similar ways.

The Great War would have been lost by the side which was deprived of its chlorine supply. Chlorine was essential to most of the poison gases used. Rolling clouds of chlorine were used in the earlier gas attacks. Mustard gas, phosgene, chlorpicrin — these demanded huge quantities of chlorine. At the end of the war the United States was making 100 tons of chlorine a day at the Edgewood Arsenal, besides all that private plants could furnish.

Since dry chlorine does not attack iron, it is compressed to a liquid in heavy steel cylinders for shipment.

Tests. — Minute traces of chlorine are readily detected by smell. A filter paper soaked in a solution of potassium iodide and starch turns blue in the gas. Chlorine sets the iodine free, thus:

$$2\,KI + Cl_2 \rightarrow 2\,KCl + I_2.$$

The *free* iodine then dissolves in the starch with development of a blue color.

NOTE: When an element unites with chlorine or any other element or radical in two proportions the compound with the lesser proportion of chlorine is called the -ous chloride and the other the -ic chloride. $FeCl_2$ is ferrous chloride and $FeCl_3$ is ferric chloride. Similarly Cu_2O and CuO are cuprous oxide and cupric oxide.

EXERCISE 7. — Name $FeSO_4$ and $Fe_2(SO_4)_3$.

HYDROGEN CHLORIDE

History. — Hydrogen chloride is not found in nature. Its water solution was known to the alchemists, but its preparation by the action of sulfuric acid on salt was not described until 1648 by Glauber. Its water solution was called "muriatic" acid and is still so referred to commercially. Very few uses for the acid were developed until it became cheap as a by-product of the Le Blanc soda process. A little hydrochloric acid is found in the gastric juice of the stomach.

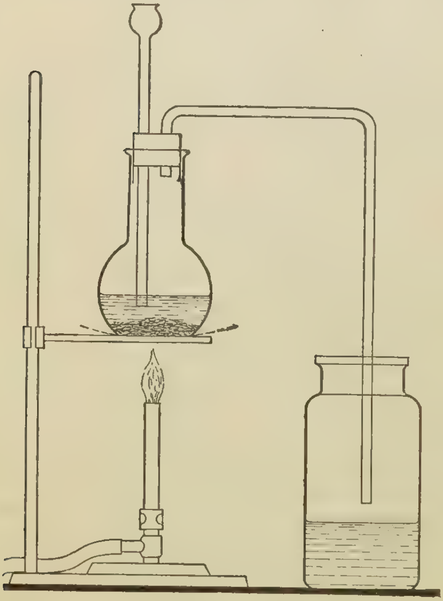


FIG. 40

Preparation. — Under Chlorine we have already mentioned the union of hydrogen and chlorine in the light to form hydrogen chloride. This action is explosive, but a jet of hydrogen can be burned quietly in an atmosphere of chlorine.

The greatest laboratory and commercial method of preparation is the treatment of any suitable chloride (sodium chloride is the cheapest) with concentrated sulfuric acid. In practice there is less frothing if the acid is slightly diluted. As shown in Fig. 40 the delivery tube should not quite touch the surface of the water. The gas is so soluble that otherwise water might rush back into the generator:

$$(1)\ \mathrm{NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl.}$$

If an excess of salt is used and the temperature raised higher the reaction is somewhat different:

$$(2)\ \mathrm{2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl.}$$

In (1) sodium hydrogen sulfate is formed and in (2) sodium sulfate (Glauber's salt).

In (1) the hydrogen chloride escapes as gas because it is insoluble in the concentrated sulfuric acid. If, however, rather dilute acid be used, the hydrogen chloride dissolves in the water. When a saturated solution of sodium-hydrogen sulfate in water is mixed with concentrated hydrochloric acid, minute cubes of sodium chloride are precipitated.

$$(3)\ \mathrm{NaHSO_4 + HCl \rightarrow H_2SO_4 + NaCl.}$$

This reaction is the exact reverse of (1), so evidently we cannot attribute either to chemical affinity alone. Here the salt precipitates (and the reaction proceeds to the right) because common salt is rather insoluble in concentrated hydrochloric acid. Of course the little crystals are still in contact with sulfuric acid, but the contact is not one millionth as effective as if the salt were really in solution — that is, subdivided into something like single molecules.

The conditions of (1) are therefore radically changed when dilute sulfuric acid is used.

$$\mathrm{NaCl + H_2SO_4 \leftrightarrows NaHSO_4 + HCl}$$

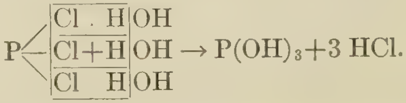
The reaction becomes reversible because there is sufficient water to dissolve the hydrogen chloride. Since it is then in good contact with the sodium hydrogen sulfate, there is nothing to hinder reaction to the left. No gas escapes. It is an impossible method for securing the evolution of hydrogen chloride.

Any metallic chloride serves as well as a source of hydrogen chloride, if it is soluble. Any acid will do if it is less volatile than the hydrogen chloride. For example, H_2F_2, hydrofluoric acid, would be driven off on heating, thus stopping the formation of the hydrogen chloride. The acid used must not react with the desired hydrogen chloride as would nitric or any other oxidizing acid. Phosphoric might seem as good as sulfuric acid, since it also has a higher boiling point than most acids, but unfortunately it reacts too slowly. Sulfuric acid is always used because it is cheap, is less volatile than hydrogen chloride (or most acids, in fact) and does not react with hydrogen chloride.

EXERCISE 8. — Complete

$FeCl_2 + \text{dilute } H_2SO_4 \rightarrow$
$FeCl_2 + \text{conc. } H_2SO_4 \rightarrow$
$KCl + H_3PO_4 \rightarrow$
$NaCl + H_2F_2 \rightarrow$
$AlCl_3 + \text{conc. } H_2SO_4 \rightarrow$

The chlorides of some non-metals react with water to form hydrogen chloride, an example of hydrolysis:



In the manufacture of nitric acid from sulfuric acid and sodium nitrate a by-product is sodium-hydrogen sulfate, $NaHSO_4$. To some extent this is now utilized by heating with salt:

$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl.$$

Both the products are valuable, while previously the sodium hydrogen sulfate was a drug on the market.

Physical Properties. — Hydrogen chloride is a colorless gas of choking odor, enormously soluble in water. One volume of water dissolves 455 volumes of the gas at 15° and 760 mm. The solution is called hydrochloric acid. The gas "fumes" in moist air by condensing the invisible moisture into visible droplets of solution. The gas is somewhat heavier than air; one liter weighs 1.642 g. At 0° it is liquefied by 28 atmospheres' pressure, but at $-84°$ one atmosphere liquefies it. This is, then, its boiling point. It freezes at $-112.5°$ and its critical temperature is 52°.

When a concentrated solution is heated it loses hydrogen chloride more rapidly than water until the concentration falls to 20.2 per cent. Then the rest of the liquid distils unchanged at 110°. This product is called the acid of *constant boiling point*. If very dilute hydrochloric acid be boiled, steam passes off more rapidly than hydrogen chloride, until the concentration rises to 20.2 per cent. It was once thought this indicated the existence of a compound of hydrogen chloride and water, but by merely changing the pressure the composition of the distillate changes. The "chemically pure" acid has a specific gravity of 1.2 and contains 37 per cent hydrogen chloride and 63 per cent water by weight.

Exercise 9. — How many grams of the gas in 850 cc. of "C. P." hydrochloric acid?

Chemical Properties. — As a dry gas hydrogen chloride is not very active, but in water solution it ranks as one of the "strongest" acids. Like all acids, its solution is sour and turns blue litmus paper red.

The metals more active than copper displace hydrogen from hydrochloric acid:

$$Fe+2\,HCl \rightarrow FeCl_2+H_2.$$

Oxides of the metals react with it to form water and a chloride of the metal:

$$Ca\boxed{O+2\,H}Cl \rightarrow H_2O+CaCl_2.$$

Hydroxides of the metals (bases) react with hydrochloric acid to form water and metallic chlorides.

$$Na\boxed{OH+H}Cl \rightarrow H_2O+NaCl,$$

$$Ca\boxed{(OH)_2+2\,H}Cl \rightarrow 2\,H_2O+CaCl_2.$$

The base and acid can be mixed in such proportions that the solution is no longer sour nor soapy, nor does it affect litmus. We say the acid has *neutralized* the base and vice versa. Soluble bases turn red litmus paper blue.

Nitric acid oxidizes hydrogen chloride into water and chlorine. Another product, nitrosyl chloride, NOCl, is also formed:

$$HNO_3+3\,HCl \rightarrow 2\,H_2O+NOCl+Cl_2.$$

A mixture of three volumes of concentrated hydrochloric acid and one volume of concentrated nitric acid is called *aqua regia* because it dissolves gold. Chlorine is continually being released from the mixture and in its nascent state is very active, converting metals to chlorides. It is more efficient in attacking metals and salts than either acid alone.

That hydrogen chloride is a reducing agent is shown by the fact that it can be oxidized.

Uses. — Hydrochloric acid is used to form many chlorides. Many metals, all metallic oxides, and some salts react with it to form chlorides:

$$\begin{gathered}CaCO_3+2\,HCl \rightarrow H_2O+CO_2+CaCl_2,\\ Na_2SO_3+2\,HCl \rightarrow H_2O+SO_2+2\,NaCl,\\ AgNO_3+HCl \rightarrow HNO_3+AgCl.\end{gathered}$$

In the third reaction the silver chloride formed is insoluble and therefore gives a precipitate if formed in a solution. It is one of the three insoluble chlorides, the other two being mercurous chloride and lead chloride. They are worth remembering.

Hydrogen chloride has its greatest use as a source of chlorine by oxidation.

It is used, also, to clean metals (reacting with the oxide, rust).

Test. — A solution turning blue litmus red and forming a white precipitate of silver chloride when silver nitrate is added must contain hydrogen chloride. As a gas it can be detected by holding a drop of silver nitrate solution on a glass rod in the air. A milkiness in the drop is a test, confirmed by the reddening of moist blue litmus paper.

Exercise 10. — When hydrogen chloride (in solution) is electrolyzed, equal volumes of hydrogen and chlorine are obtained. Also when equal volumes of hydrogen and chlorine are combined, two volumes of hydrogen chloride are formed. How does this confirm Gay-Lussac's law?

Exercise 11. — Balance:

$$\begin{array}{l}PbO+HCl \rightarrow\\ Pb_2O_3+HCl \rightarrow\\ Pb_3O_4+HCl \rightarrow\\ PbO_2+HCl \rightarrow\\ MnO+HCl \rightarrow\\ Mn_2O_3+HCl \rightarrow\\ Mn_3O_4+HCl \rightarrow\\ MnO_2+HCl \rightarrow\\ Na_2CO_3+HCl \rightarrow\\ CuO+HCl \rightarrow\\ KOH+HCl \rightarrow\end{array}$$

Exercise 12. — How many liters of chlorine are released by heating 2 Kg. of red lead, Pb_3O_4, with enough hydrochloric acid to complete the reaction?

CHAPTER X

BROMINE, IODINE, FLUORINE, AND THE HALOGEN ACIDS

	AT. WGT.	MELTING PT.	BOILING PT.	COLOR AND STATE
Fluorine (F)	19.00	−223°	−187.0°	Pale-yellow gas
Chlorine (Cl)	35.46	−102°	−33.6	Greenish-yellow gas
Bromine (Br)	79.92	−7	63.0°	Reddish-brown liquid
Iodine (I)	126.92	113°	184.4°	Violet-black solid

The Halogen Family. — Chlorine, bromine, iodine and fluorine exhibit such close resemblances as elements and in their compounds that they are grouped as a family of "halogens." They are the least like the metals of all the elements. The name *halogen* means "salt former," given because they all unite with metals to form salts such as sodium chloride.

History. — The history of chlorine has already been given. Davy demonstrated its elementary nature in 1810, and very soon afterwards iodine was made by Courtois, who heated the ash of seaweed with concentrated sulfuric acid, obtaining violet vapors. This method, with some modification, is still used. Courtois did not know what he had made, but in 1814 Gay-Lussac proved that the new substance was an element and gave it the name "iodine" from the Greek for "violet."

Liebig just missed discovering bromine when he was once given a salt residue rich in free bromine. He thought it was merely a compound of iodine and chlorine. Balard, in 1826, released bromine from a salt liquor by the action of free chlorine, the most modern method of commercial preparation we have to-day, a century later. He also treated a salt, which he later found to be potassium bromide, with concentrated sulfuric acid and manganese dioxide. Even this method is still in use.

As early as 1670 chemists knew that the mineral fluorspar (CaF_2), when warmed with concentrated sulfuric acid, produced a gas that attacked glass. Scheele suspected this mineral to be the calcium salt of some acid, but not until 1807 was the acid (H_2F_2) prepared by Gay-Lussac. All efforts to release the element fluorine from this acid failed, due to its great activity, until Moissan in 1886 isolated it by electrolyzing potassium fluoride in solution in liquid hydrofluoric acid. The solution was contained in a cooled U-tube. Later a copper tube was found to serve as well. The coating of copper fluoride first formed protected the rest of the copper. Stoppers of calcium fluoride were used.

Occurrence. — The halogens are too active to occur free in nature. Chlorine in sodium chloride is the most common.

Bromine (Br) in the form of magnesium bromide ($MgBr_2$) and sodium bromide (NaBr) is far less abundant, but it is found with the sodium chloride in sea water, in the great salt layers at Stassfurt, Germany, and in the salt brines of Michigan and West Virginia. It occurs elsewhere, but these are the chief commercial sources. The Dead Sea contains much magnesium bromide.

Iodine (I), until recent years, was wholly obtained from seaweed ash by heating with concentrated sulfuric acid and manganese dioxide. Now nearly all of it is obtained from the beds of Chili saltpeter ($NaNO_3$), where it is found to the extent of 0.2 per cent as sodium iodate ($NaIO_3$). Recently there has been some extraction of iodine on a small scale from the giant kelp on the California coast. A small amount of an organic iodine compound, iodothyrin, is found in the thyroid gland of man. Where we are deficient in this, goiter or cretinism develops. Extracts of a sheep's thyroid gland have been administered successfully as a remedy.

Fluorine (F) is found as fluorspar (CaF_2), cryolite (Na_3AlF_6) and apatite ($3\ Ca_3(PO_4)_2 \cdot CaF_2$). Cryolite occurs in Greenland and is of great importance in making the metal aluminum.

Preparation. — Electrolysis is a successful commercial method of preparation only for chlorine. There is no commercial demand for fluorine for obvious reasons, and bromine and iodine can be made by cheaper methods.

Oxidation of hydrogen chloride has been given as one of the great methods of preparing chlorine. The preparation of fluorine by a similar method is impossible. The oxidation of hydrogen fluoride is represented by the following equation:

$$O + H_2F_2 \rightarrow H_2O + F_2.$$

Fluorine reacts vigorously with water to form oxygen and hydrogen fluoride; therefore the above reaction is reversed too readily to permit separation of the fluorine.

But oxidation serves well in the preparation of bromine and iodine. The same reaction given for chlorine applies.

A mixture of sodium bromide, manganese dioxide and concentrated sulfuric acid is heated moderately. The vapors of bromine are condensed in a cooled flask (Fig. 41).

$$2\,NaBr+3\,H_2SO_4+MnO_2 \rightarrow 2\,NaHSO_4+MnSO_4+2\,H_2O+Br_2$$
$$2\,NaI+3\,H_2SO_4+MnO_2 \rightarrow 2\,NaHSO_4+MnSO_4+2\,H_2O+I_2$$

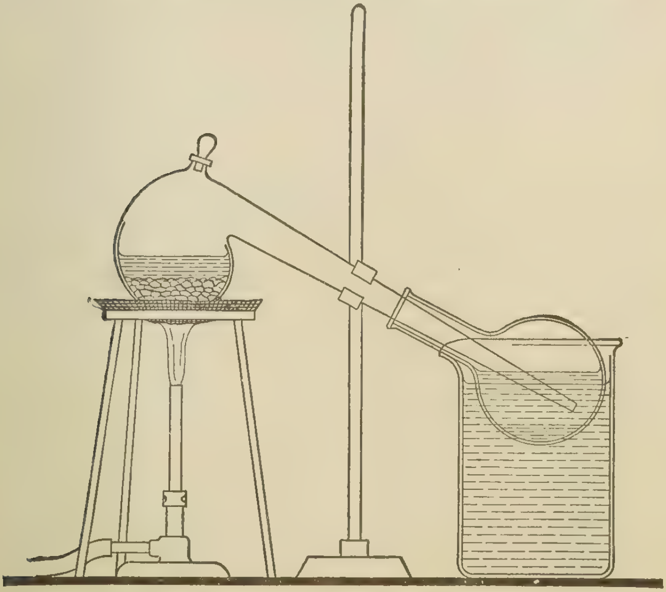


FIG. 41

In other words, the oxidation of hydrogen bromide ($2\,HBr+O \rightarrow H_2O+Br_2$) is a part of the mechanism of the reaction.

Fluorine has the greatest affinity for the metals, chlorine next, bromine third, and iodine least. So the element chlorine displaces bromine from any bromide and iodine from any iodide. Commercial use is made of this fact:

$$2\,NaBr+Cl_2 \rightarrow 2\,NaCl+Br_2,$$
$$MgBr_2+Cl_2 \rightarrow MgCl_2+Br_2.$$

Chlorine is allowed to rise through a tower down which a brine containing sodium or magnesium bromide is trickling. A clever modification is the electrolysis of a salt brine, just enough to release the bromine but not the chlorine. Iodine may be released from the sodium iodide of kelp ash in the same way.

The sodium iodate in Chili saltpeter is decomposed by sodium bisulfite:

$$2\ NaIO_3 + 5\ NaHSO_3 \rightarrow 3\ NaHSO_4 + 2\ Na_2SO_4 + H_2O + I_2.$$

Exercise 1. — Would iodine displace bromine from a bromide?

Properties. — In addition to the table of properties at the head of this chapter it might be mentioned that we know nothing of the solubility of fluorine in water because it reacts so rapidly. At 0° chlorine dissolves in 100 cc. of water to the extent of 1.49 g., bromine 4.3 g., and iodine 0.32 g. Bromine forms a hydrate, $Br_2.10\ H_2O$, similar to $Cl_2.8\ H_2O$.

A most striking relation of properties to atomic weight is apparent from an examination of the table at the beginning of the chapter. The weights increase in the order fluorine, chlorine, bromine, iodine, and the melting point (freezing point) rises with increase in weight. The heaviest is a solid at room temperatures, bromine only a liquid and the lighter ones gases. Even the depth of color increases with weight. The boiling point rises in the same order. But the activity decreases as the elements grow heavier, except towards oxygen. Fluorine refuses to unite with oxygen; the oxides of chlorine are unstable, one of them exploding below 100°; bromine has no known oxides, and even iodine pentoxide (I_2O_5) is not difficult to decompose. All the halogens unite directly with phosphorus. Iodine and white phosphorus unite vigorously with the evolution of heat, bursting into flame in fact.

At ordinary temperature these four elements are diatomic, as Cl_2, etc. But at high temperatures they dissociate into molecules made up of single atoms. At 1700° the density of iodine corresponds to a molecular weight of 127, the same as the weight of one atom. At 1043° the density of the vapor (compared to air) is 7.01, which means that only 25 per cent of the molecules have dissociated and the other 75 per cent are still I_2.

Exercise 2. — At 1275° the density of iodine vapor is 5.82. What percentage of the molecules have separated into two atoms each? Remember Avogadro's law.

Iodine dissolves in many organic liquids such as chloroform, carbon disulfide, hydrocarbons (in all these with violet color), alcohol and ether (in these two with brown color). Although but slightly soluble in water, it dissolves readily in an aqueous solution of sodium or potassium iodide:

$$KI + I_2 \leftrightarrows KI_3.$$

The potassium triiodide (KI_3) is rich red and very soluble. That its formation is an equilibrium reaction can be shown by testing for free iodine with starch paste (blue solution formed). By using up the little free iodine (as by adding "hypo") the equilibrium is continuously disturbed to the left and the red color fades.

Exercise 3. — How do we know that there can be no more than 0.32 g. per 100 cc. of *free* iodine on the left of the above equation with the temperature near 0°?

A quantity of iodine in the open air volatilizes on evaporation. On heating it changes rapidly into violet vapors without passing through the liquid stage. Such a change is called *sublimation.* Iodine is sublimed to separate it from impurities.

Uses of the Halogens. — Fluorine is too difficult to make and keep for any practical use. Ammonium fluoride is a disinfectant for brewery vessels. Sodium fluoride is an effective wood preservative. Sodium hydrogen fluoride is much used in polishing granite. Magnesium silicofluoride ($MgSiF_6$) is soluble and finds use in hardening concrete. Chlorine, as stated previously, is of great industrial importance. Bromine is used in making some aniline dyes, in making potassium bromide (a valuable nerve sedative), and, in the form of silver bromide, is the sensitive material on photographic plates. Bromine was used in the Great War to make "tear gases" such as bromacetone. Iodine is rather expensive, finding application as silver iodide in photography, as iodides in medicine, and in the manufacture of some dyes. Iodoform (CHI_3) is a valuable antiseptic. Tincture of iodine, an alcoholic solution of the element, is of great service in medicine. As a laboratory reagent in quantitative analysis iodine is well known.

The Halogen Hydrides. — H_2F_2, HBr, and HI resemble HCl in many respects. All are colorless gases, irritating in odor, extremely soluble in water, forming acid solutions and fuming in moist air.

They may all be made by direct union of the elements, but with certain differences:

$H_2+F_2 \rightarrow H_2F_2$ explosively, even in the dark,
$H_2+Cl_2 \rightarrow 2\ HCl$ quietly in the dark, explosively in bright light,
$H_2+Br_2 \rightarrow 2\ HBr$ if heated and passed over platinum gauze,
$H_2+I_2 \rightarrow 2\ HI$ if heated much hotter and passed over platinum gauze.

In practice hydrogen fluoride is made by warming concentrated sulfuric acid and calcium fluoride in a lead vessel as glass is attacked:

$$CaF_2+H_2SO_4 \rightarrow CaSO_4+H_2F_2.$$

We might reasonably expect hydrogen bromide to be made by treating a bromide with concentrated sulfuric acid:

$$(1)\quad NaBr+H_2SO_4 \leftrightarrow NaHSO_4+HBr.$$

Yet when we do this, in addition to the colorless, fuming hydrogen bromide, we observe a red-brown gas. A paper wet with starch and potassium iodide solutions turns blue. From this and the color and the choking, irritating odor we decide that bromine was released, evidently oxidized out of the hydrogen bromide by the concentrated sulfuric acid. When dilute sulfuric acid is used, no gas escapes and no color appears. The reaction becomes reversible as with chlorides because of the great solubility in water of hydrogen bromide. But it is noteworthy that no red-brown color can be seen — dilute sulfuric acid is not an oxidizing agent. With concentrated acid equation (1) is followed by (2):

$$(2)\quad 2\ HBr+H_2SO_4 \rightarrow 2\ H_2O+SO_2+Br_2$$

Each molecule of hot, concentrated H_2SO_4 loses one oxygen atom to the hydrogen of the bromide and leaves H_2SO_3, which is unstable, yielding H_2O+SO_2.

We might also have expected to make hydrogen iodide by warming some iodide with concentrated sulfuric acid:

$$NaI+H_2SO_4 \rightarrow NaHSO_4+HI.$$

But very little fuming in moist air shows the presence of but little hydrogen iodide. Much violet vapor proves to be free iodine. As with the bromide, concentrated sulfuric acid oxidizes the hydrogen iodide:

$$2\ HI+H_2SO_4 \rightarrow H_2O+SO_2+I_2.$$

A vile odor of rotten eggs indicates the presence of hydrogen sulfide (H_2S), so some molecules of sulfuric acid must have given up all four oxygen atoms for the work of oxidation. This really means that hydrogen iodide is a more vigorous reducer than hydrogen bromide:

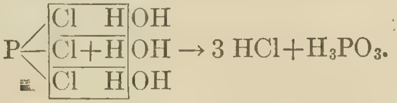
$$8\ HI + H_2SO_4 \rightarrow 4\ H_2O + 4\ I_2 + H_2S.$$

So we discard the sulfuric acid method as unsuitable for hydrogen bromide or iodide. Phosphoric acid would be excellent, as it is not very volatile and not an oxidizing acid, but unfortunately the action is too slow. If the temperature is raised to increase the speed the product decomposes:

$$2\ HI \rightarrow H_2 + I_2.$$

The red phosphorous method, however, serves us very well. It is recalled that chlorine and phosphorus unite to form a chloride, PCl_3, that is hydrolyzed by water:

$$PCl_3 + 3\ H_2O \rightarrow P(OH)_3 + 3\ HCl$$
$$PBr_3 + 3\ H_2O \rightarrow P(OH)_3 + 3\ HBr,$$
$$PI_3 + 3\ H_2O \rightarrow P(OH)_3 + 3\ HI,$$



$$P\begin{cases} Cl\quad H\,OH \\ Cl + H\,OH \\ Cl\quad H\,OH \end{cases} \rightarrow 3\ HCl + H_3PO_3.$$

The reactions with phosphorous tribromide and phosphorous triiodide are similar. Red phosphorus, slightly moistened, is put in a flask with a delivery tube attached, and bromine cautiously added from a dropping funnel. The heat of the reaction volatilizes much bromine, which is caught by a little moist red phosphorus in a U-tube through which the gases pass (Fig. 42). The colorless hydrogen bromide is led into

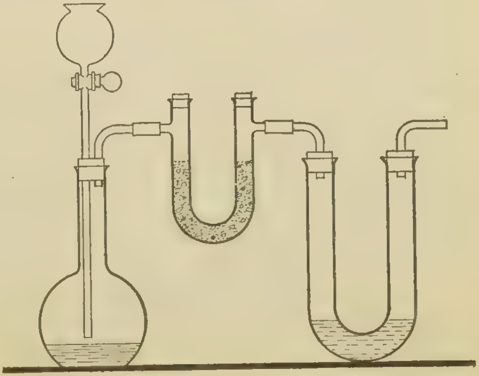


FIG. 42

water, forming hydrobromic acid. Of course the first reaction was as follows:

$$2\,P+3\,Br_2 \rightarrow 2\,PBr_3.$$

With hydrogen iodide the water is dropped on a mixture of red phosphorus and iodine. Hydrogen sulfide passed into water containing iodine in suspension reacts as follows:

$$H_2S+I_2 \rightarrow 2\,HI+S.$$

The sulfur may be filtered out and the colorless liquid concentrated by boiling.

Bromine reacts with benzene to form hydrogen bromide:

$$C_6H_6+Br_2 \rightarrow C_6H_5Br+HBr.$$

Properties of the Halogen Acids. — These colorless, extremely soluble gases have all been liquefied at low temperatures, but are not acid unless mixed with water. The explanation of this is given in the chapter on Ionization. The water solutions are called hydrobromic acid, hydriodic acid, and hydrofluoric acid. As such they are very strong acids and conduct electricity well. They react with most metals with displacement of hydrogen, and react with metallic oxides and hydroxides as does hydrochloric acid:

$$\begin{aligned} Zn+2\,HBr &\rightarrow ZnBr_2+H_2,\\ MgO+2\,HBr &\rightarrow MgBr_2+H_2,\\ NaOH+HI &\rightarrow NaI+H_2O. \end{aligned}$$

Exercise 4. — How make $CaBr_2$, KI, CuF_2?

From the foregoing discussion it is clear that we have not oxidized hydrogen fluoride at all by any reagent; that hydrogen chloride is not oxidized by concentrated sulfuric acid but can be attacked by several better oxidizing agents; that hydrogen bromide is so easily oxidized that even hot concentrated sulfuric acid does it; and that hydrogen iodide is still more easily oxidized. A solution of hydriodic acid soon turns red because free oxygen of the air reacts with part of it.

$$\begin{aligned} &(1)\ 4\,HI+O_2 \rightarrow 2\,H_2O+2\,I_2\\ &(2)\ I_2+HI \leftrightarrows HI_3 \end{aligned}$$

Reaction (2) is similar to the solution of iodine in potassium iodide.

Hydrogen bromide has a critical temperature of 91° C. When liquefied it boils at −68.5° and freezes at −86°. One volume of water dissolves 612 volumes of the gas under standard conditions. The "constant boiling acid" (at 126°) contains 48 per cent hydrogen bromide.

Hydrogen iodide boils at −36° and freezes at −51°. One volume of water dissolves 450 volumes of the gas at 10°. The constant boiling acid (at 128°) contains 57 per cent hydrogen iodide. Both hydrogen bromide and iodide are much heavier than air.

Exercise 5. — From their formulas calculate the weight of one liter hydrogen bromide and iodide and get the density in terms of air.

Hydrogen fluoride is a colorless liquid boiling at 19°. It freezes at −92.3°. The gas is very poisonous. One volume of water dissolves 302 volumes of hydrogen fluoride. The constant boiling acid (120°) contains 35 per cent of the compound. The density of the vapor of hydrogen fluoride indicates a molecular weight of 40 and hence the formula H_2F_2. This is confirmed by the existence of such salts as KHF_2. Above 100° the density indicates a formula of HF.

Uses of the Acids. — Hydrobromic and hydriodic acids have little commercial use, but hydrofluoric acid is valuable because it etches glass. Common glass is a mixture of the silicates of sodium and calcium.

$$Na_2SiO_3 + 3\ H_2F_2 \rightarrow Na_2F_2 + SiF_4 + 3\ H_2O$$
$$CaSiO_3 + 3\ H_2F_2 \rightarrow CaF_2 + SiF_4 + 3\ H_2O$$

Bottles, thermometers, etc., are marked by covering with a film of paraffin, cutting through a design, and then exposing the vessels to the fumes or the liquid acid. The wax is not attacked but the glass is etched where the scratches expose it. Later the vessel is washed and the wax melted. A 30 per cent solution of the acid is commonly used. Rubber, lead or ceresin-wax bottles are the common containers, since this acid cannot be kept in glass bottles.

This acid is used in aiding glass polishers to make "cut" glass, in cleaning sand from metal castings, and in removing silica from straw used for hats so as to make the straw more flexible. The action on silica or acid is

$$SiO_2 + 2\ H_2F_2 \rightarrow 2\ H_2O + SiF_4.$$

Silicon tetrafluoride (SiF_4) is a colorless gas.

Exercise 6. — Suppose that to-morrow a new halogen is isolated with an atomic weight of 214. Describe its properties, how the acid is made, and the properties of the acid. Call the element "Doline" (Do) and the acid hydrogen dolide or dolidic acid (HDo).

Exercise 7. — Make a four-column chart on which you compare the four halogens in solubility, action on water, and other properties. Compare their acids in ease of oxidation. Give tests for the four elements and the four acids.

CHAPTER XI

THE OXYGEN ACIDS OF THE HALOGENS

Chlorine and iodine do not combine directly with oxygen, but their oxides can be made by indirect methods. Bromine and fluorine have no oxides and fluorine has no place in this chapter at all, for it forms neither oxide nor oxygen acid.

Hypochlorous Acid. — The key reaction of this entire chapter has been studied in the chlorine chapter:

$$(1)\quad Cl_2+H_2O \leftrightarrows HCl+HClO.$$

This is shown to be a reversible reaction by tests for acidity and for the presence of free chlorine. Blue litmus paper is reddened before it is bleached, but the solution is only weakly acid. The presence of dissolved chlorine is proved by the yellow color of the mixture, by odor and by the reaction on a starch-potassium iodide paper. (What is this reaction?) The hypochlorous acid (HClO) is a powerful oxidizing agent and so the equilibrium is disturbed to the right by the presence of any oxidizable substance. Addition of a base also disturbs the equilibrium to the right by conversion of the two acids into salts:

$$(2)\quad NaOH+HCl \rightarrow H_2O+NaCl,$$
$$(3)\quad NaOH+HClO \rightarrow H_2O+NaClO.$$

In other words there is no free chlorine left in the solution after sufficient base has been added. The bleaching power of such a solution was first observed by Berthollet in 1785. Chlorine passed into sodium hydroxide solution forms, then, sodium chloride and sodium hypochlorite (NaClO), sometimes called Javelle water.

If to the mixture represented by (2) and (3) sufficient dilute sulfuric acid be added, both hydrochloric and hypochlorous acids are formed.

$$(4)\quad NaCl+H_2SO_4 \leftrightarrows NaHSO_4+HCl$$
$$(5)\quad NaClO+H_2SO_4 \leftrightarrows NaHSO_4+HClO$$
$$(6)\quad HCl+HClO \leftrightarrows H_2O+Cl_2.$$

Reaction (6) inevitably follows from (4) and (5). It is simply the reverse of (1). No wonder chlorine can be detected after acidifying "Javelle water."

To prepare hypochlorous acid pure and anhydrous has not been found possible. But aqueous solutions are prepared by a clever use of the difference in strength of hydrochloric and hypochlorous acids. If to chlorine water, equation (1), powdered calcium carbonate, ($CaCO_3$), be added, it reacts only with the stronger acid, hydrochloric, leaving the very feeble hypochlorous acid untouched:

$$2\,HCl + 2\,HClO + CaCO_3 \rightarrow CaCl_2 + H_2O + CO_2 + 2\,HClO.$$

Since the latter is volatile it can be distilled off with some water. The dilute distillate can be concentrated to some extent.

Another device is to start with neutralized chlorine water, that is, a mixture of sodium chloride and sodium hypochlorite. If nitric acid, for example, be added in amounts not sufficient to react with both salts, it will be found to have reacted first with the sodium hypochlorite:

$$NaCl + NaClO + HNO_3 \rightarrow NaCl + NaNO_3 + HClO.$$

The hypochlorous acid along with some water may then be distilled off. It is safer to use the weak boric acid instead of nitric, for a large excess could be added before any hydrochloric acid would be formed.

Hypochlorous acid is a more energetic oxidizing agent than oxygen because more energy is released by the oxidation of a given weight of some reducing substance in the first case than in the second. Hypochlorous acid is a valuable bleaching agent from the very fact that it bleaches by oxidation of coloring matter.

On concentrating this unstable acid too far it decomposes into water and its anhydride, chlorine monoxide.

$$2\,HClO \leftrightarrows H_2O + Cl_2O.$$

An *anhydride* of an acid is an oxide that reacts with water to form the acid and it may be represented by the formula of the acid less the elements of water. SO_3 is the anhydride of H_2SO_4. To get the anhydride of nitric acid we must subtract H_2O from 2 HNO_3.

Exercise 1. — What is the anhydride of carbonic acid (H_2CO_3)? Of phosphoric acid (H_3PO_4)?

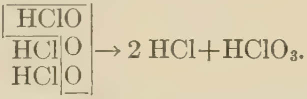
In the Chlorine chapter we learned that hypochlorous acid decomposes slowly in the sunlight:

$$2\ HClO \rightarrow 2\ HCl + O_2.$$

Even its salts are somewhat unstable, decomposing slowly thus:

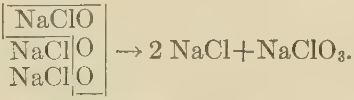
$$2\ NaClO \rightarrow 2\ NaCl + O_2.$$

This reaction is catalyzed by the hydroxide of cobalt. If chlorine gas be passed into a solution of sodium hydroxide to which a little cobalt salt has been added, a steady stream of oxygen escapes.



$$\left|\begin{array}{l|l} \hline \text{HClO} & \\ \hline \text{HCl} & \text{O} \\ \text{HCl} & \text{O} \end{array}\right| \rightarrow 2\ HCl + HClO_3.$$

The free acid decomposes in another way, as shown by the equation above. The sodium salt reacts in similar fashion, especially in a hot, concentrated, slightly acid solution, and sodium chlorate is formed rapidly:

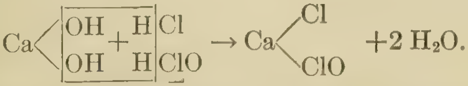


$$\left|\begin{array}{l|l} \hline \text{NaClO} & \\ \hline \text{NaCl} & \text{O} \\ \text{NaCl} & \text{O} \end{array}\right| \rightarrow 2\ NaCl + NaClO_3.$$

This remarkable reaction reminds us of three brothers, each too poor to boast. But two self-sacrificing ones gave all their money to the third, enriching him to a degree that brought lustre to the family name. Most absurd but a clear parallel to the auto-oxidation of the 3 NaClO.

Exercise 2. — In what three ways can hypochlorous acid decompose?

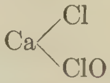
Bleaching Powder. — Lime may be used instead of sodium hydroxide to react with chlorine and, if done in the dry form, a *bleaching powder* results:



$$Ca\Big<\left|\begin{array}{ll|l} \hline OH & + \ H & Cl \\ OH & \ \ \ \ H & ClO \\ \hline \end{array}\right. \rightarrow Ca\Big<\begin{array}{l} Cl \\ ClO \end{array} + 2\ H_2O.$$

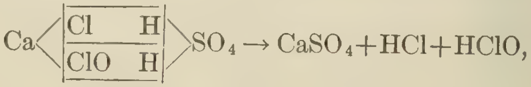
In all probability a little water in the dry powder reacts with chlorine to form the two acids, as in equation (1). Of course they promptly neutralize the lime and more water is formed.

Bleaching powder is sometimes called "chloride of lime," which should refer only to $CaCl_2$. It was once thought to be a mixture of an equal number of molecules of $CaCl_2$ and $Ca(OCl)_2$. This is incorrect, however, because alcohol dissolves nothing from it and yet calcium chloride is very soluble in alcohol. Furthermore, calcium chloride is very deliquescent, but commercial bleaching powder is not. It is evidently a mixed salt of both hydrochloric and hypochlorous acids, as indicated by the formula



$\mathrm{Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{ClO}\end{matrix}\right.$.

When acidified the reaction resembles the one with acidified Javelle water:

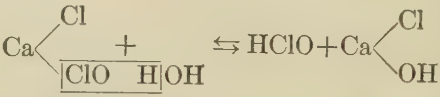


$$\mathrm{Ca}\left\langle\begin{matrix}\boxed{\mathrm{Cl}\quad\mathrm{H}}\\ \boxed{\mathrm{ClO}\quad\mathrm{H}}\end{matrix}\right\rangle\mathrm{SO_4}\rightarrow\mathrm{CaSO_4+HCl+HClO},$$

$$\mathrm{HCl+HClO}\leftrightarrows\mathrm{H_2O+Cl_2}.$$

As stated before, it is the hypochlorous acid that does the bleaching. The question naturally arises: How is it that bleaching powder always smells of chlorine when no acid has been added? The fact is this odor is not due to chlorine but to chlorine monoxide (Cl_2O). The small amount of carbonic acid always present in the air (from $H_2O+CO_2 \leftrightarrows H_2CO_3$) is able to release the hypochlorous acid but not the hydrochloric acid. Hypochlorous acid is unstable and to some extent decomposes into water and its anhydride, chlorine monoxide, which smells like chlorine.

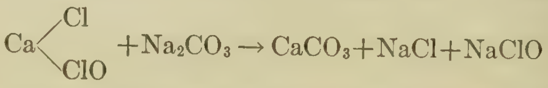
It is also probable that the reaction of water with bleaching powder (hydrolysis) releases a little hypochlorous acid and basic calcium chloride:



$$\mathrm{Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \qquad +\\ \boxed{\mathrm{ClO}\quad\mathrm{H}}\mathrm{OH}\end{matrix}\right.\leftrightarrows\mathrm{HClO+Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{OH}\end{matrix}\right.$$

For reasons developed later very little hydrochloric acid is released. The foregoing discussion explains why clothes can be bleached by wetting with a solution of bleaching powder and hanging in the air and sunlight.

The best modern laundry practice discourages the direct use of bleaching powder and uses Javelle water made by the reaction:



$$\mathrm{Ca}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{ClO}\end{matrix}\right.+\mathrm{Na_2CO_3}\rightarrow\mathrm{CaCO_3+NaCl+NaClO}$$

The insoluble calcium carbonate is filtered off. The equivalent of this solution is made by still more modern laundry practice in another way. Common salt solution is electrolyzed with electrodes very close together, so that the sodium hydroxide formed at the cathode reacts with the chlorine water at the anode. Of course the chlorine water contains two acids, but these are neutralized by the base formed at the cathode. The resulting sodium hypochlorite is an effective bleaching agent:

$$HCl + HClO + 2\ NaOH \rightarrow 2\ H_2O + NaCl + NaClO.$$

It is claimed that this solution is cheaper, more convenient and that less is used. At all events the public is deeply concerned in the utmost possible reduction in amounts of "bleach" used in laundries. Wool and silk are attacked so much that they are bleached by gentler agents, and even cotton and linen are weakened perceptibly. Therefore it is important that the "bleach" be thoroughly rinsed out of the fabrics. It is always possible to neutralize the remaining "bleach" by adding the harmless "hypo" used by photographers. The reaction will be discussed in the chapter on sodium.

The manufacture of bleaching powder is a huge industry. Chlorine is passed over three-inch layers of slaked lime ($Ca(OH)_2$) which are stirred occasionally. In theory the product should contain 49 per cent of "available" chlorine (liberatable by acids), but in practice from 35 to 38 per cent is the best obtained, about two thirds efficiency.

In the table given below is a fine illustration of the law of Multiple Proportions.

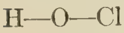
NOMENCLATURE

HCl	Hydrochloric Acid	$NaCl$	Sodium Chloride	HBr	Hydrobromic Acid	HI	Hydriodic Acid
$HClO$	Hypochlorous Acid	$NaClO$	Sodium Hypochlorite	$HBrO$	Hypobromous Acid	HIO	Hypoiodous Acid
$HClO_2$	Chlorous Acid	$NaClO_2$	Sodium Chlorite	....		....	
$HClO_3$	Chloric Acid	$NaClO_3$	Sodium Chlorate	$HBrO_3$	Bromic Acid	HIO_3	Iodic Acid
$HClO_4$	Perchloric Acid	$NaClO_4$	Sodium Perchlorate	....		HIO_4	Periodic Acid

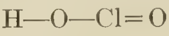
In a way, chloric acid is used as the norm in naming these acids. An acid with more oxygen is called perchloric; the one with a little less is called chlorous acid; one with still less hypochlorous acid; and the one with no oxygen at all has a different style of name. In the corresponding salts the ending "ate" goes with the ending "ic" in the oxygen acid and the ending "ite" with the ending "ous" in the acid. There are only three oxides of chlorine, namely chlorine monoxide (Cl_2O), chlorine dioxide (ClO_2) and chlorine heptoxide (Cl_2O_7). There are no oxides of bromine. Iodine has two oxides, the pentoxide (I_2O_5) and the heptoxide (I_2O_7).

The *structural formulas* of the Oxygen Acids of Chlorine are worth noting.

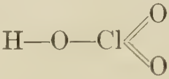
Hypochlorous Acid



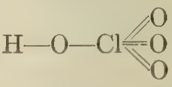
Chlorous Acid



Chloric Acid



Perchloric Acid



So far we have considered the valence of chlorine as one, but here we see that it may also be three, five, or seven. Chlorine heptoxide (Cl_2O_7) indicates a valence of seven as it should be in the anhydride of perchloric acid.

Chloric Acid. — One of the most important of the oxygen acids of the halogens is chloric acid ($HClO_3$). It can be made by the action of dilute sulfuric acid on any chlorate, preferably barium chlorate, because the by-product, barium sulfate, is insoluble and can be filtered off:

$$Ba(ClO_3)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ HClO_3.$$

In hot concentrated solution hypochlorous acid changes to some extent into chloric acid:

$$3\ HClO \rightarrow 2\ HCl + HClO_3.$$

This vigorous oxidizing acid is a colorless liquid which can be concentrated to a 40 per cent solution without decomposition if kept below 40°. It is really a more energetic oxidizing agent than ozone. If dilute hydrochloric acid and a few crystals of potassium chlorate be added to black lead sulfide, the chloric acid set free quickly turns the lead sulfide into white lead sulfate:

$$3\ PbS + 4\ HClO_3 \rightarrow 3\ PbSO_4 + 4\ HCl.$$

When a few drops of concentrated sulfuric acid are added to two or three fragments of potassium chlorate the size of grains of wheat, the chloric acid freed decomposes violently:

$$4\ HClO_3 \rightarrow 2\ H_2O + O_2 + 4\ ClO_2.$$

It is dangerous to use larger quantities. A hot wire thrust into the chlorine dioxide gas escaping causes a very violent explosion.

More important than the acid is its potassium salt ($KClO_3$). This finds use as a convenient laboratory source of oxygen and in the manufacture of fireworks, matches, dyes and explosives. It is such an effective source of oxygen that the results of its use are often startling and sometimes dangerous.

It is interesting to drop a splinter into a test tube one third full of melted potassium chlorate. So vigorous is the oxidation of the wood that it burns brilliantly under the liquid, flames shoot out of the tube and some spattering of hot liquid may result. Were the wood finely divided as sawdust or used as powdered charcoal, a dangerous explosion would result.

One chemist grinding pure potassium chlorate in a clean mortar was astonished by a loud explosion. Another mortar from the same lot produced the same result. Investigation showed that the wooden handle of the pestle had been cemented into the head by melted sulfur. The sulfur crumbled and a little fell into the potassium chlorate during grinding. The enormously rapid oxidation of sulfur was explosive.

The chlorates are more stable as a class and consequently less powerful oxidizing agents than the hypochlorites. All chlorates are at least moderately soluble in water and some are deliquescent. Sodium chlorate is much more soluble than the potassium salt, but usually serves the same purpose. In 1915 war necessity compelled the United States to make the sodium salt, as we could not import potassium salts from Germany.

Exercise 3. — The solubility of potassium chlorate at 20° is 7.5 g. per 100 cc. of water and of sodium chlorate is 99 g. per 100 cc. If to a saturated solution of sodium chlorate (in 100 cc. of water) an equivalent amount of potassium chloride is added, how many grams of potassium chlorate would be precipitated?

$$NaClO_3 + KCl \rightarrow NaCl + KClO_3.$$

The simplest method of making potassium chlorate is to pass chlorine into a hot, concentrated solution of potassium hydroxide:

$$3\ Cl_2 + 6\ KOH \rightarrow KClO_3 + 5\ KCl + 3\ H_2O.$$

This equation sums up several steps. First chlorine reacts with water, then the acids formed are neutralized by the base and finally potassium hypochlorite is partly converted into the desired chlorate — as it does rapidly if the solution is hot:

$$3\ KClO \rightarrow 2\ KCl + KClO_3.$$

Potassium hydroxide is not cheap, yet in this method five sixths of it is almost wasted, becoming the far cheaper potassium chloride. An economy long ago adopted was to pass chlorine first into a suspension of lime in water and thus secure the cheaper calcium salts:

$$6\ Ca(OH)_2 + 6\ Cl_2 \rightarrow 5\ CaCl_2 + Ca(ClO_3)_2 + 6\ H_2O,$$
$$Ca(ClO_3)_2 + 2\ KCl \rightarrow CaCl_2 + 2\ KClO_3.$$

Here the five sixths waste is in cheap calcium hydroxide and only enough potassium chloride is added later to convert the calcium chlorate into potassium chlorate. The latter salt is easily separated from the more soluble calcium chloride.

The most modern method of manufacture is to electrolyze potassium chloride, letting the solutions at the anode and cathode mix. This first produces the hypochlorite, but if the solutions are hot and concentrated the chlorate is the final product.

Perchloric Acid. — When potassium chlorate is kept melted for some time potassium perchlorate is formed as an intermediate product, although raising the temperature still higher decomposes the perchlorate into oxygen and potassium chloride:

$$4\ KClO_3 \rightarrow KCl + 3\ KClO_4.$$

On cooling the soluble potassium chloride is easily separated from the rather insoluble potassium perchlorate. As might be expected, perchloric acid can be made by treatment of the perchlorate with sulfuric acid:

$$KClO_4 + H_2SO_4 \rightarrow KHSO_4 + HClO_4.$$

Distilled under greatly reduced pressure the pure acid has been obtained as a colorless, unstable liquid. Serious explosions have occurred in the making. The acid often decomposes spontaneously with violence. However, a 60 per cent solution, quite safe to handle, is now largely used in the quantitative determination of potassium, replacing the very expensive platinic chloride reagent.

Perchloric acid is such a powerful oxidizing agent that in contact with easily oxidizable material explosions may result.

Oxides of Chlorine. — Chlorine monoxide (Cl_2O), the dioxide (ClO_2), and the heptoxide (Cl_2O_7) are unstable, even explosive, substances of considerable oxidizing power. Further details concerning them may be obtained from reference books.

Chlorine heptoxide (Cl_2O_7), a colorless, unstable oil, is the anhydride of perchloric acid, from which it is made by the action of cold phosphorus pentoxide (P_2O_5) in abstracting the elements of water.

Hypobromous and Hypoiodous Acids. — There is good evidence that bromine and iodine react with water like chlorine to a lesser degree:

$$Cl_2+H_2O \leftrightarrows HCl+HClO,$$
$$Br_2+H_2O \leftrightarrows HBr+HBrO,$$
$$I_2+H_2O \leftrightarrows HI+HIO.$$

Bromine or iodine water to which a base has been added has oxidizing properties only less powerful than the similar chlorine preparation.

Bromic and Iodic Acids. — Bromic acid ($HBrO_3$) can be made by oxidizing bromine with hypochlorous acid. Iodic acid (HIO_3) is usually made by oxidizing iodine with nitric acid. The reaction

$$2\ KClO_3+I_2 \rightarrow 2\ KIO_3+Cl_2$$

shows that iodine displaces chlorine from oxygen compounds, although we have learned that chlorine displaces iodine from other compounds. A very little nitric acid greatly aids the above reaction. Iodic acid is a white crystalline substance, a strong oxidizing agent, and at 170° begins to lose water with formation of its anhydride (I_2O_5).

During the Great War iodine pentoxide was used in the analysis of carbon monoxide and as a gas mask absorbent for carbon monoxide.

Periodic Acid. — This acid and some of its salts are known. Similar compounds of bromine do not exist. Sodium periodate ($NaIO_4$) is found in Chili saltpeter.

Relative Stability. — Of the acids those with most oxygen are most stable. Their salts are all more stable than the acids. Another order of stability is

HIO_3 most stable, $HClO_3$, less, $HBrO_3$, least.

For comparison,

HCl most stable, HBr less, HI least.

Exercise 4. — How prepare a water solution of hypochlorous acid two ways?

Exercise 5. — What are the anhydrides of all the oxygen acids of the halogens?

Exercise 6. — Why is it dangerous to add concentrated sulfuric acid to several grams of potassium chlorate?

Exercise 7. — Give the evidence showing that bromine and iodine react with water similarly to chlorine.

CHAPTER XII

IONIZATION

Introduction. — In a previous chapter we have said that acids, bases and salts differ in certain respects from other substances. A brief restatement of their nature may be clarifying.

Acids all contain hydrogen, although all hydrogen compounds are not acids, sugar for example. Acid solutions in water ordinarily taste sour, turn blue litmus red, release carbon dioxide from carbonates, and react with most metals with displacement of hydrogen.

The common bases are compounds of a metal with oxygen and hydrogen. In water solution they turn red litmus blue. Such metallic hydroxides as those of sodium, potassium and calcium ($NaOH$, KOH, $Ca(OH)_2$) have already been mentioned.

A salt is formed by the reaction between an acid and a base, the other product being water. Salts may be formed in several other ways to be described later.

$$NaOH + HCl \rightarrow NaCl + H_2O,$$
$$Ba(OH)_2 + H_2SO_4 \rightarrow BaSO_4 + 2\ H_2O.$$

Here the sodium chloride and barium sulfate are salts.

Evidences of Ionization. — The examples of *double decomposition* already studied exhibit an exchange of groups or radicals when acids, bases or salts are mixed in aqueous solution:

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2\ NaCl,$$
$$H_2SO_4 + Ba(NO_3)_2 \rightarrow BaSO_4 + 2\ HNO_3.$$

In these two equations we observe a tendency for the sulfate radical ($-SO_4$) to break away from sodium or hydrogen and unite with barium. Before the sulfate group can unite with barium there must be a dissociation of sodium sulfate and also of barium chloride. The easy and instant exchange of the same radicals in such reactions leads us to suspect a preliminary decomposition of acids, bases and salts into radicals as soon as dissolved in water.

So the name "double decomposition" is appropriate. In displacement we have a similar separation into radicals:

$$Zn + H_2SO_4 \rightarrow H_2 + ZnSO_4.$$

One of the most convincing pieces of evidence of such dissociation in water is found in the *abnormally large values for freezing point lowering, boiling point rise, and osmotic pressure of aqueous solutions of acids, bases and salts.* A solution of a gram molecular weight of sugar, glycerine, etc., in 1000 g. of water freezes at −1.86°. It makes no difference whether heavy sugar molecules or light alcohol molecules are dissolved, — the only consideration is *number of dissolved particles.* Doubling the concentration doubles the freezing point lowering. After observing this it is astonishing to learn that a solution containing one gram molecular weight of sodium chloride per 1000 g. of water freezes at a temperature approaching *twice* 1.86° below zero. Since this solution apparently contains exactly the same number of molecules as the sugar solution (a gram molecular weight of each taken) and since the only influence on freezing point lowering is *number* of dissolved particles, we are forced to the only possible conclusion, namely that some of the sodium chloride molecules must have broken down, dissociated into smaller particles, thus accounting for more particles than the original number of molecules. Now there is only one way for such a simple compound to dissociate, for there are only two atoms in each molecule of sodium chloride:

$$NaCl \rightarrow Na + Cl.$$

Obviously, if all the salt molecules split into two parts, the original number of molecules would be doubled and the solution would freeze at exactly $2 \times 1.86°$ below zero. This complete dissociation is approximated only in very dilute solutions. Evidently the less water present the less the dissociation and with no water (dry salt) only molecules are found.

The student at once admits the necessity of accounting for more particles than indicated by a gram molecular weight and admits that this explanation accounts for them, but he doesn't see how ordinary sodium can exist in contact with water. For that matter he is skeptical about the presence of ordinary chlorine in salt water. Chlorine water is greenish yellow, poisonous and a powerful oxidizing agent, and he knows by experience that salt water has none of these properties. He remembers that metallic sodium reacts violently with water, but there is nothing exciting to be seen when salt is dissolved in water.

The answer to these doubts is found in the facts of electrolysis, but before discussing that topic there are a few more facts to consider at this point.

A solution containing one gram molecular weight of sulfuric acid has a freezing point lowering approaching three times 1.86°. The inference is that each molecule dissociates into three parts, probably as follows:

$$H_2SO_4 \rightarrow H + H + SO_4.$$

The sulfate group does not disintegrate, for a solution of copper sulfate ($CuSO_4$) indicates the formation of only two parts per molecule, one of course being copper and the other the sulfate group. In all these dissociations the same radicals form as those taking part in double decomposition, a very significant point.

After all, this conception of dissociation is not without precedent. When ammonium chloride is heated and 22.4 liters of its vapor weighed, we find the data indicate a much smaller molecular weight than corresponds to the formula NH_4Cl. Fortunately, there are simple tests which show a dissociation of the hot molecules:

$$NH_4Cl \leftrightarrows NH_3 + HCl.$$

This behavior of ammonium chloride once made chemists question Avogadro's hypothesis.

The fraction dissociated can be calculated from the freezing point of the solution. Suppose one tenth of a gram molecular weight of sodium chloride (5.85 g. NaCl) were dissolved in 1000 cc. of water and the solution froze at $-0.356°$. If no molecules dissociated, the freezing point lowering would have been 0.186° $\left(\frac{1.86°}{10}\right)$, so the *excess lowering* produced by extra particles beyond the ordinary molecules must be 0.356° less 0.186° or 0.170°. Therefore $\left(\frac{0.170}{0.186}\right)$ or 91.4 per cent of the molecules were dissociated.

$$8.6 \text{ per cent, } HCl \leftrightarrows (H) + (Cl), \text{ } 91.4 \text{ per cent.}$$

Exactly the same proof of the dissociation of acids, bases and salts in aqueous solution can be found in their abnormally great boiling point rise and osmotic pressure.

Exercise 1. — Give this proof for boiling point rise.

Electrolysis. — Although water was decomposed by the electric current as early as 1800 (Nicholson and Carlisle), most of our knowledge of electrolysis, and its terms, we owe to Faraday, the great English chemist and physicist, 1834.

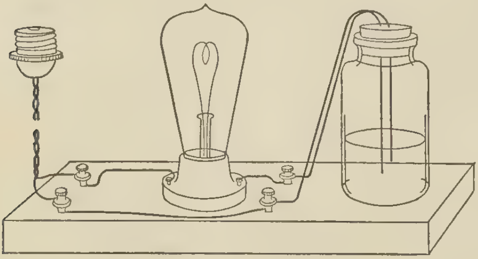


Fig. 43 *a*

When two metallic plates (electrodes) are placed in a solution and connected with a source of current we have an electrolytic cell. If a lamp be placed in the circuit, as in Fig. 43 *a*, we can observe by its glow when current is passing. An ammeter measures current more accurately. Place the electrodes in pure water and connect with the ordinary lighting circuit. The failure of the lamp to glow shows that little or no current passes. Evidently water is a poor conductor. Now add sugar or glycerine or alcohol to the water and stir. Even these solutions do not conduct the current. But add dilute sulfuric acid or some soluble salt or base and the lamp glows. In fact any acid, base, or salt dissolved in the water of the cell described will conduct the current. The remarkable fact is that *only acids, bases and salts* (which we therefore call *electrolytes* or *ionogens*) will do this; all other substances are called non-electrolytes.

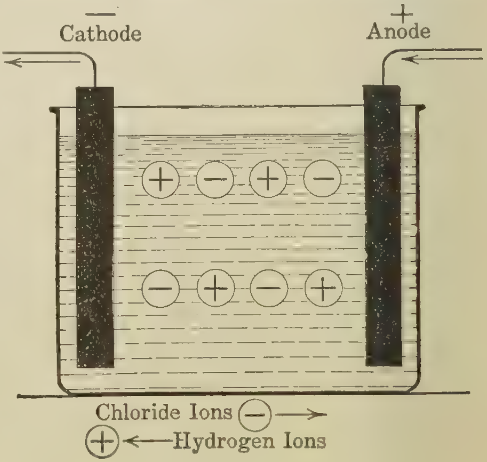


Fig. 43 *b*

Suppose in the cell of Fig. 43 *b* we use a solution of hydrochloric acid and pass a direct current through the circuit. The electrode where the current enters is called the ***anode*** and the one by which it leaves the ***cathode.*** Ions attracted to the anode are called *anions*, while those attracted to the cathode are termed *cations*. The passage of the current merely keeps the anode positively charged and the cathode negatively charged. Hydrogen escapes at the cathode and chlorine at the anode. In other words, hydrochloric acid is electrolyzed. Hydrogen particles from the entire solution travel to the cathode and are there released. Why, unless they are attracted? The cathode is a negatively charged strip of metal and consequently attracts oppositely charged bodies. The conclusion is that the hydrogen particle is simply an atom carrying a positive charge of electricity. In this form it is soluble in water but on contact with the negative electrode its charge is neutralized and the plain hydrogen atoms then unite in pairs to form ordinary hydrogen gas molecules which escape. The chlorine particles move from all parts of the solution to the anode, or positive electrode. This attraction must be due to the presence of a negative charge on the chlorine particle or atom. On contact with the electrode the charge on the chlorine atom is neutralized and common chlorine escapes and may be detected by the usual tests. Both the hydrogen and chlorine are *primary products of electrolysis.*

When sulfuric acid is electrolyzed, its hydrogen is liberated at the negative electrode, as with all acids, but the sulfate radical is not found as a molecular substance at the positive electrode. Instead, oxygen escapes. If the experiment be performed in a U-tube, it can be shown that sulfuric acid accumulates around the positive electrode and diminishes in concentration around the other electrode. Evidently the sulfate radical is attracted by the positive electrode because of the negative charge carried by the radical. After discharge the simple radical, unable to exist in molecular form, reacts with water:

$$2\,SO_4+2\,H_2O \rightarrow 2\,H_2SO_4+O_2.$$

Of course this sulfuric acid of the equation, a *secondary product of electrolysis*, is itself electrolyzed and so on indefinitely.

Copper sulfate is electrolyzed with a red deposit of metallic copper on the cathode and escape of oxygen at the anode. Potassium iodide, on electrolysis, shows the color of iodine at the anode and yields the usual blue with a drop of starch paste. At the cathode hydrogen escapes, and if a drop of colorless phenolphthalein solution be added a splendid purple color develops, indicating the formation of a base. Potassium hydroxide is the only one possible. The positively charged potassium atom, after attraction to the cathode and discharge there, inevitably reacts with water as in the following equation:

$$2\ K+2\ H_2O \rightarrow H_2+2\ KOH.$$

Silver nitrate, on electrolysis, yields a deposit of metallic silver on the cathode (a primary product) while oxygen and nitric acid are formed at the anode (secondary products). Evidently the silver nitrate dissociated into Ag and NO_3 radicals. On discharge at the positive pole the NO_3 radical reacts with water:

$$4\ NO_3+2\ H_2O \rightarrow O_2+4\ HNO_3.$$

Exercise 2. — Explain how a spoon is silver plated.

From these facts of electrolysis, and others, the Swedish chemist, Arrhenius, deduced his great theory of electrolytic dissociation. In launching this theory Van't Hoff, the Dutch chemist, and Ostwald, the German chemist, aided materially.

The Ionic Theory. — *Acids, bases and salts in aqueous solution dissociate into atoms or groups of atoms which carry charges of electricity.*

This explains the possibility of the existence of sodium particles without the expected action on water. A sodium atom carrying a positive charge of electricity is called an ***ion*** and is soluble in water, invisible, and does not react with water. Similarly a chlorine atom carrying a negative charge of electricity is called an ion and is a very different substance from greenish-yellow, poisonous chlorine. It is colorless, soluble in water and non-poisonous. A solution of copper sulfate is blue because of the copper ion. When such a solution is electrolyzed the soluble, positively charged, blue ion is discharged at the negative electrode and becomes common red, insoluble, metallic copper. Truly an electric charge makes a vast difference. A sulfate radical ($-SO_4$) is incapable of separate existence except when loaded with negative electricity.

There is no excess of either positive or negative electricity on the ions dissociating from each molecule of an electrolyte. That is, there must be an equal number of positive and negative charges on the anions and cations.

How else can we explain the *electroneutrality of solution?* The salty ocean is neither positive nor negative or there would be very little ocean bathing. If we allow one positive charge to a hydrogen ion ($\overset{+}{\mathrm{H}}$), then there must be one negative charge to a chloride ion ($\overset{-}{\mathrm{Cl}}$) and the ionization of hydrogen chloride is

$$\mathrm{HCl} \rightarrow \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}}.$$

It follows then that in the ionization of sodium chloride the sodium ion must carry one positive charge to equal that on the chloride ion. A series of equations follows, each a logical development from the preceding (except the fourth):

$$(1)\ \mathrm{NaCl} \rightarrow \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}}$$

$$(2)\ \mathrm{CuCl_2} \rightarrow \overset{++}{\mathrm{Cu}} + \overset{-}{\mathrm{Cl}} + \overset{-}{\mathrm{Cl}}$$

$$(3)\ \mathrm{CuSO_4} \rightarrow \overset{++}{\mathrm{Cu}} + \overset{--}{\mathrm{SO_4}}$$

$$(4)\ \mathrm{HNO_3} \rightarrow \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{NO_3}}$$

$$(5)\ \mathrm{AgNO_3} \rightarrow \overset{+}{\mathrm{Ag}} + \overset{-}{\mathrm{NO_3}}$$

$$(6)\ \mathrm{Fe(NO_3)_3} \rightarrow \overset{+++}{\mathrm{Fe}} + \overset{-}{\mathrm{NO_3}} + \overset{-}{\mathrm{NO_3}} + \overset{-}{\mathrm{NO_3}}$$

Faraday's Law.[1] — Faraday gave us an experimental basis for ascribing a definite number of charges to each ion. He found that *when a gram equivalent weight of any metal or hydrogen has been liberated from a compound by electrolysis, exactly* 96,540 *coulombs of electricity passed through the solution.*

For example, this same quantity of electricity can set free from electrolyte solutions gram equivalent weights of H (1.008 g.), of Ag (107.88 g.), of Cu $\left(\frac{63.57}{2}\text{ g.}\right)$, and of Al $\left(\frac{27.1}{3}\text{ g.}\right)$. Of course equivalent quantities of the negative ions are being discharged at the same time in electrolysis. That is, one gram equivalent weight of hydrogen chloride is decomposed by 96,540 coulombs of electricity, for this means that one gram equivalent weight of hydrogen and one gram equivalent weight of chlorine are released simultaneously.

---

[1] The coulomb is the unit of quantity of electricity, as the liter is a unit of quantity of water.

Electrolysis is merely an attraction and discharge of ions, so there must be 96,540 coulombs of electricity on each gram atomic weight of hydrogen ions or of silver ions. But this quantity of electricity discharges only half of one gram atomic weight of copper $\left(\frac{63.57}{2}\text{ g. Cu}\right)$ so there must be $2 \times 96{,}540$ coulombs on a whole gram atomic weight of copper and, by similar logic, $3 \times 96{,}540$ coulombs on a whole gram atomic weight of aluminum. In other words, this 96,540 coulombs is the unit charge. In the case of hydrogen ion it is represented by $\overset{+}{\mathrm{H}}$. For others it is

$$\overset{+}{\mathrm{Na}},\ \overset{+}{\mathrm{K}},\ \overset{+}{\mathrm{Ag}},\ \overset{++}{\mathrm{Cu}},\ \overset{+++}{\mathrm{Al}},\ \overset{+}{\mathrm{Cl}},\ \overset{-}{\mathrm{NO_3}},\ \overset{--}{\mathrm{SO_4}},\ \overset{---}{\mathrm{PO_4}},\ \text{etc.}$$

Exercise 3. — How many coulombs of electricity are required to decompose 45 g. of copper sulfate?

Exercise 4. — This number of charges on the ion exactly parallels valence. The valence of the phosphate radical (PO_4) is three. How many negative charges does it carry?

The source of these great charges (ionization occurs *before* any electric current is turned on) is a matter of question to the student. We now have convincing evidence that an atom is composed of a positive nucleus and a number of negative charges of electricity. When sodium chloride ionizes, the sodium atom *loses one negative charge to the chloride atom.* This loss of a negative charge leaves the sodium atom positive relatively, and it becomes an ion ($\overset{+}{\mathrm{Na}}$) while the addition of a negative charge to the chlorine atom makes it a negative ion ($\overset{-}{\mathrm{Cl}}$). This reminds us of the relative enrichment of a debtor when some friend assumes a dollar debt for him. Suppose the debtor owned $40 and was also in debt $40. His actual wealth is nothing, but after his friend assumes a one dollar debt the debtor is really worth one dollar, his financial status is +1. These negative charges are called *electrons*, so we speak of atoms gaining or losing *electrons*.

When sodium and chlorine unite to form sodium chloride a great deal of heat is liberated, an exothermic reaction. Naturally this same amount of heat should be absorbed in decomposing sodium chloride. Yet on dissolving this salt in water no large quantity of heat is absorbed (with great temperature lowering) as expected. The required energy is accounted for by this transfer of electrons.

Ionization Equilibrium.—Another annoying question in the mind of the student is this: if oppositively charged ions exist in the same solution, free to move, why do they not attract and discharge each other? They do. But as fast as they unite to form new molecules some other molecules ionize and we merely have a condition of ionic equilibrium which can be disturbed like any other equilibrium:

$$NaCl \leftrightarrows \overset{+}{Na} + \overset{-}{Cl}.$$

This method of writing the equation shows that there are both molecules and ions present. In more dilute solutions the percentage of molecules ionized is greater. This is reasonable, for dilution keeps the ions further apart, but has no effect on the action of molecules in breaking apart. At about 0.001 N nearly all salts are almost completely ionized, in fact 0.1 N hydrochloric acid is 93 per cent ionized. Solutions of electrolytes when diluted (up to a certain limit) conduct electricity better than when more concentrated. This is to be expected, for it is the ions that carry the current. For each electrolyte in solution there is a definite concentration that contains the greatest number of these conducting ions per cc. The passage of electricity along a wire is sometimes likened to the flow of water in a pipe, but through a solution it is carried by separate moving ions as water is carried in buckets. The general effect is that of flow.

The equilibrium in any ionization varies with the electrolyte. Some acids and bases ionize but little. In alcohol there is much less ionization than in water, while in carbon disulfide and benzene there is practically none. Hydrogen chloride dissolves in toluene, but such a solution has no acid properties whatever and does not conduct electricity.

The velocity of migration of ions when attracted to the electrodes is not very great. At 18° under a potential difference of one volt with electrodes one centimeter apart the swiftest ion of all, $\overset{+}{H}$, moves only 10.8 cm. per hour, $\overset{-}{OH}$ moves 5.6 cm. per hour, Cu 1.6 cm., $\overset{+}{K}$ 2.05 cm. and Cl 2.12 cm. This migration may be observed by electrolyzing the blue solution of copper sulfate in a U-tube. It is best to have a layer of a colorless electrolyte such as potassium nitrate in the upper part of each arm. The blue of the copper ion slowly moves to the cathode and away from the anode.

Exercise 5. — What would be the weight of 22.4 liters of ammonium chloride vapor if every molecule dissociated into $NH_3 + HCl$?

Exercise 6. — Give a convincing array of evidence for the ionic theory.

Summary. — 1. Acids, bases, and salts are the only substances that exchange radicals as in double decomposition, and these same radicals are separated from aqueous solution by electrolysis.

2. Acids, bases, and salts lower the freezing point, raise the boiling point, and produce osmotic pressure in water to an extent not accounted for by the number of molecules. Therefore some of these molecules dissociate (ionize) into additional particles, which produce the abnormal values.

3. Solutions of acids, bases, and salts are the only substances that conduct electricity, with resulting decomposition. Solid metals conduct without decomposition.

4. Electrolysis is preceded by ionization and is merely an attraction of radicals to charged plates and release at these plates.

5. The ionic theory explains electrolysis by describing the dissociation radicals of electrolytes (or ionogens) as atoms or groups of atoms carrying electric charges. The cations with positive charges are attracted to the negative plate or cathode and there discharged, while the anions are attracted to the positive anode and discharged. The discharged radicals are released as primary products of electrolysis or react with the water to form secondary products.

6. By Faraday's law equal quantities of electricity liberate equivalent quantities of the ions. A gram equivalent weight of any element or radical carries 96,540 coulombs of electricity and therefore this amount is required to discharge and liberate it.

7. The number of positive and negative charges on the ions from each molecule is equal, as shown by the fact that electrolyte solutions as a whole show no trace of electrification. The number of charges on an ion is the same as its valence.

8. The source of the charges on the ions is the transfer of electrons (negative charges of about 1/1800 the mass of the hydrogen atom) from the metallic radicals to the non-metallic ones.

9. Ions continually attract, meet, and discharge ions of opposite charge to form molecules, which in turn are continually ionizing. An equilibrium between molecules and ions exists, depending on the particular electrolyte used, the dilution, the solvent and temperature.

CHAPTER XIII

APPLICATIONS OF THE IONIC THEORY

Conductivity and Ionization. — The ability of a solution to conduct electricity (its conductivity) depends upon the number of ions present, the number of electric charges carried by each and the velocity of ionic migration (see page 145 for comparative velocities). There is a striking parallel between the conductivity, freezing point lowering, and chemical activity of normal solutions of acetic, sulfuric, and hydrochloric acid. As Cady states it, under similar conditions (surface, temperature, etc.) normal acetic acid releases 1 cc. of hydrogen when in contact with zinc in exactly the same time that the zinc discharges 65 cc. of hydrogen from normal sulfuric acid and 100 cc. from normal hydrochloric acid. Under these conditions hydrochloric acid is a hundred times as active as acetic. A normal solution of hydrochloric acid freezes at nearly twice 1.86° below zero, while a normal solution of acetic acid freezes at only a trifle below $-1.86°$. Normal acetic acid has but little more effect on freezing point lowering than has sugar. Normal hydrochloric acid conducts electricity well, sulfuric acid about two thirds as well, while normal acetic is only a very poor conductor.

The conclusion from these facts is that hydrochloric acid in normal solution ionizes very well, most of the molecules dissociate, while in normal acetic acid a very small fraction of the molecules have dissociated.

At greater dilutions even acetic ionizes to a greater degree. The molecular conductivity of any electrolyte increases with dilution up to a maximum and then remains the same. This means that finally all the molecules yield conducting ions. For example, the molecular conductivity of hydrochloric acid at 18° is 379 when diluted beyond $\frac{N}{2000}$; this is the maximum and corresponds to complete ionization. At $\frac{N}{10}$ this acid has a conductivity of 351.

Evidently $\frac{351}{379}$ or 93% of the molecules have ionized at this concentration. This is a valuable method of measuring the fraction ionized.

In a battery jar (Fig. 44) place two long metal strips as electrodes and fill three fourths full with water. With a long-stemmed dropping funnel introduce concentrated hydrochloric acid under the lighter water so that there is almost no mixing. After placing a lamp in the circuit turn on the current. The lamp scarcely glows. Now stir the solutions, thus greatly diluting the acid. The bright glowing of the lamp shows the formation of many more ions at the greater dilutions. It is only ions that conduct in solutions.

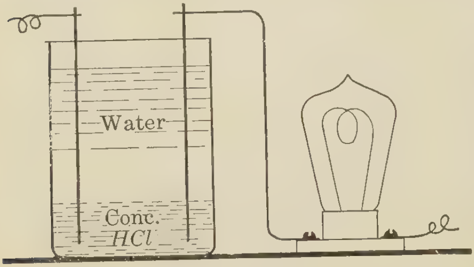


Fig. 44

The Fraction Ionized. — A table giving the percentage ionization of several acids, bases, and salts is invaluable as a picture of their relative activity. In a general way this property depends on the degree of ionization.

Fraction Ionized in 0.1 N Solutions at 18°

Acids		
HCl		0.93
HBr	N/2	.90
HNO_3		.93
$HMnO_4$ Permanganic	N/2	.93
$H_2SO_4 \rightarrow \overset{+}{H}+\overset{+}{H}+\overset{--}{SO_4}$		.61
$H.C_2H_3O_2$, Acetic		.013
$H_2CO_3 \rightarrow \overset{+}{H}+\overset{--}{HCO_3}$		.0017
$H_2S \rightarrow \overset{+}{H}+\overset{-}{HS}$		.0007
HCN, Prussic		.0001
$H.H_2BO_3$ Boric		.0001
H_2O		.000,0001

Bases		
KOH		0.91
NaOH		.91
$Ba(OH)_2$		.81
NH_4OH		.013
$N(CH_3)_4OH$	N/16	.96
H_2O		.000,0001

Salts	
KCl	0.86
NaCl	.85
NH_4Cl	.85
$BaCl_2$	.76
$CaCl_2$	.76

KBr		.86
$NaNO_3$		.83
KNO_3		.82
$Sr(NO_3)_2$		.72
$AgNO_3$		.81
K_2SO_4		.72
$MgSO_4$		.45
$ZnSO_4$		.41
$CuSO_4$		.40
$NaC_2H_3O_2$		.79
$Cd(NO_3)_2$	N	.56
$CdBr_2$	N	.16
$HgCl_2$		.01
$Hg(CN)_2$		A trace

From this table we learn that "strong" acids, such as hydrochloric and nitric, are 93 per cent ionized in 0.1 N solution. In fact it is this high percentage ionization that makes them so active chemically or "strong." Sulfuric acid is only moderately strong with 61 per cent ionized. Concentrated sulfuric acid is more destructive to animal and plant tissue, but only 1 per cent of ordinary 95 per cent sulfuric acid is ionized. In such concentrated form it has certain dehydrating and oxidizing properties not observed in the dilute form, but as an acid its activity is less. Acetic acid (found in vinegar) is "weak" with only 1.3 per cent ionized. Carbonic acid is very weak, as we might have known since it is present in the lungs and mouth. Prussic acid is a powerful poison, but as an acid it is still weaker than carbonic. Hydrogen sulfide (H_2S) is an offensive gas, but its water solution is only very faintly acidic.

The common bases, sodium and potassium hydroxide, are the strongest. Calcium hydroxide is not included, because it is not soluble to the extent of 0.1 N solution. In 0.015 N solution it is 90 per cent ionized. Ammonium hydroxide seems strong enough to the nose, but it is really a weak base, only 1.3 per cent being ionized. However, when the four hydrogens are replaced by the organic group, methyl (CH_3), it becomes one of the strongest bases known. The name of this substituted ammonium hydroxide is formidable, tetramethylammonium hydroxide, $N(CH_3)_4OH$, but it means something to the organic chemist.

Salts, with two or three exceptions, are all "strong," or highly ionized in dilute solution. The cadmium halides and some mercuric salts are almost in a separate class.

Acids containing more than one ionizable hydrogen atom to the molecule such as sulfuric, carbonic or phosphoric, ionize by stages with increasing dilution. With a certain amount of water a given weight of sulfuric acid may first ionize thus:

$$H_2SO_4 \leftrightarrows \overset{+}{H} + \overset{-}{HSO_4}.$$

Addition of more water makes it possible for the second hydrogen to ionize. The algebraic balance of positive and negative charges is still correct:

$$\overset{-}{HSO_4} \leftrightarrows \overset{+}{H} + \overset{--}{SO_4}.$$

With carbonic acid (H_2CO_3) there is almost none of the second hydrogen ionized. Phosphoric acid (H_3PO_4) throws off the first hydrogen easily, the second to a very limited degree and the third almost not at all.

There is a possibility of some confusion as to the amount of ionizable hydrogen in 0.1 N solutions of a strong acid and a weak acid. Hydrochloric acid attacks zinc about one hundred times as fast as does acetic, but give the acetic time enough and the same weights of hydrogen will be released by equal volumes of 0.1 N acids. The reason is that ionization is a case of equilibrium:

$$98.7\%\ \text{H.acetate} \leftrightarrows \overset{+}{H} + \overset{-}{\text{acetate}},\ 1.3\%.$$

If zinc displaces these hydrogen ions from solution, the equilibrium is continuously disturbed to the right (there can be no reversing to the left with hydrogen ions gone) and finally all the acetic acid molecules have ionized. Thus equal volumes of the same normality of all acids contain exactly equal weights of "potential" hydrogen ions, but the strong acids contain much more of "actual" hydrogen ions at any instant than do the weaker acids.

Types of Electrolytes. — It is now clear that an acid is any substance that, in water solution, yields hydrogen ions. So it is hydrogen ion, common to all acids, that is responsible for the sour taste, the attack on bases, carbonates and the reddening of litmus. Monobasic acids yield only one hydrogen ion per molecule, as HCl, HNO_3, $H.C_2H_3O_2$ and HCN. Dibasic acids yield two hydrogen ions per molecule, as H_2SO_4. Obviously H_3PO_4 is a tribasic acid. From the formula of acetic acid ($C_2H_4O_2$) it might be thought that four hydrogen atoms should ionize. Only one breaks off as an ion even at great dilutions. The other three are attached differently inside the molecule and are not even potential ions. So we often write the formula $H.C_2H_3O_2$ or even H.acetate.

A base is any substance that yields hydroxyl ions in water solution. A *monacid* base yields but one hydroxyl ion per molecule, as KOH, NaOH and NH_4OH. But $Ca(OH)_2$ is a *diacid* base and $Al(OH)_3$ a *triacid* base. We admit that it is only in neutralization that all three hydroxyl groups of $Al(OH)_3$ could be made to ionize, but they are potential ions. Salts we defined previously as one of the products of the neutralization of an acid by a base, the other being water. They may also be defined as the product of the union of any positive ion except $\overset{+}{H}$ ion, with any negative ion except $\overset{-}{OH}$ ion. Normal salts are formed by replacing all the ionizable hydrogen of an acid by a metal as in Na_2SO_4 or K_3PO_4. Acid salts are formed by replacing only part of the ionizable hydrogen of acids by a metal, as in $KHSO_4$ or Na_2HPO_4. Basic salts result when only part of the hydroxyl groups of a base are neutralized by an acid, as in $Ca\begin{matrix}\diagup OH\\ \diagdown Cl\end{matrix}$. Mixed salts have, in a single molecule, different metals, as $NaKSO_4$, or different negative radicals, as bleaching powder, $Ca\begin{matrix}\diagup Cl\\ \diagdown ClO\end{matrix}$.

The positive ion is nearly always a metal with a few such exceptions as hydrogen and the ammonium ion, $(\overset{+}{NH_4})$. The negative ion never contains a metal alone.

Of course we can form any salt by the simple device of mixing the oppositely charged ions. For example, to form barium sulfate we need only take a solution of *any barium salt* (because these will furnish $\overset{++}{Ba}$) and mix it with any *soluble sulfate* (because these furnish $\overset{--}{SO_4}$). It is a matter of comparative indifference what the other ions accompanying these are. Mix $BaCl_2$ and Na_2SO_4. Solutions of these are already ionized, so we mix four kinds of ions:

$$\overset{++}{Ba}+\overset{-}{Cl}+\overset{-}{Cl}+\overset{+}{Na}+\overset{+}{Na}+\overset{--}{SO_4}\rightarrow BaSO_4+\overset{+}{Na}+\overset{+}{Na}+\overset{-}{Cl}+\overset{-}{Cl}.$$

The student at once asks why $BaSO_4$ was written as a molecule on the right. It is so insoluble that it precipitates, leaving the ions of sodium chloride in solution. So the effect is practically this:

$$\overset{++}{Ba}+\overset{--}{SO_4}\rightarrow BaSO_4.$$

Were barium sulfate soluble we should have only its ions in solution in equilibrium with the others and on evaporating we should have a mixture of four salts. There are several methods of forming salts and a list of them will be useful.

1. Direct union of some elements.
2. Action of an acid on some metals.
3. Action of an acid on metallic oxides.
4. Action of an acid on metallic hydroxides (neutralization).
5. Action of an acid on carbonates or sulfites or sulfides or any substance yielding one gaseous product.
6. Double decomposition depending on insolubility of one product.
7. Displacement of one metal by another.
8. In general by mixing the two ions that form the salt. But to permit the separation of a pure salt the other ions must be selected with care.

Examples:

1. $2\ Na+Cl_2\rightarrow NaCl$
2. $Zn+2\ HCl\rightarrow ZnCl_2+H_2$
3. $ZnO+2\ HCl\rightarrow ZnCl_2+H_2O$
4. $Zn(OH)_2+2\ HCl\rightarrow ZnCl_2+2\ H_2O$
5. $\left\{\begin{array}{l} Na_2CO_3+2\ HCl\rightarrow 2\ NaCl+H_2O+CO_2 \\ Na_2SO_3+2\ HCl\rightarrow 2\ NaCl+H_2O+SO_2 \\ Na_2S+2\ HCl\rightarrow 2\ NaCl+H_2S \end{array}\right.$
6. $BaCl_2+Na_2SO_4\rightarrow 2\ NaCl+BaSO_4$ (Insoluble)
7. $Zn+CuSO_4\rightarrow Cu+ZnSO_4$

Colors of Solutions. — Water solutions of sodium chloride are colorless at every concentration, so we conclude that sodium ion and chloride ion as well as the molecules of sodium chloride are colorless. The sulfate ion must be colorless because sulfuric acid solutions have no color. Copper ion must be blue since dilute solutions of copper sulfate are blue. It may be objected that the blue color is due to molecules. This can't be true, however, because the dry salt, heated until all water is lost, is white and this is made up of molecules only. In some solutions each ion may have color and the molecules too. The actual color then is the resultant of a mixture of colors.

If to dry cupric bromide ($\mathrm{CuBr_2}$) a very little water be added the color is brown. With a little more water the color is green and with still more blue. The color of the dry salt must be due to molecules and with but little water the effect of molecules still predominates as brown. Now the cupric ion is blue (all dilute copper salt solutions are blue) and the bromide ion is colorless (see any solution of potassium bromide), so a very dilute solution of cupric bromide is blue since practically all the brown molecules have dissociated into blue cupric ions and colorless bromide ions. With less water there must be a concentration containing many brown molecules and many blue ions as well. Such a mixture of colors appears green.

The ionization equilibrium can be disturbed in either direction.

$$\mathrm{CuBr_2} \leftrightarrows \overset{++}{\mathrm{Cu}}+\overset{-}{\mathrm{Br}}+\overset{-}{\mathrm{Br}}$$

To the green solution add solid potassium bromide. This increase in the number of bromide ions gives more opportunities for contact with cupric ions and the reaction to the left is hastened. This increase in formation of brown cupric bromide molecules and decrease in number of blue cupric ions causes the green solution to turn brown. The equilibrium is disturbed to the right when the bromide ions are precipitated by addition of any soluble powdered lead salt to the brown solution. This decreases the number of brown molecules of cupric bromide and increases the number of blue cupric ions. The resulting color mixture is green.

Exercise 1. — To what is the color of a yellow solution of potassium chromate ($\mathrm{K_2CrO_4}$) due? The purple of potassium permanganate ($\mathrm{KMnO_4}$) in dilute solution?

Ionogen Reactions. — There are three types of double decomposition:

1. Double decomposition with both products soluble,
2. Double decomposition with one product insoluble,
3. Double decomposition with one product only slightly ionized.

As an illustration of (1) we give this:

$$\mathrm{NaNO_3+KCl \leftrightarrows NaCl+KNO_3},$$

$$\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{NO_3}}+\overset{+}{\mathrm{K}}+\overset{-}{\mathrm{Cl}} \leftrightarrows \overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{Cl}}+\overset{+}{\mathrm{K}}+\overset{-}{\mathrm{NO_3}}.$$

Now any positive ion must inevitably attract, meet and discharge any negative ion in the solution, so four different equilibrium reactions can be written:

$$\begin{array}{lcccc} \mathrm{NaNO_3} & \leftrightarrows & \overset{+}{\mathrm{Na}} & + & \overset{-}{\mathrm{NO_3}} \\ \mathrm{KCl} & \leftrightarrows & \overset{-}{\mathrm{Cl}} & + & \overset{+}{\mathrm{K}} \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & \mathrm{NaCl} & & \mathrm{KNO_3}. \end{array}$$

None of the products remain in the molecular form to any considerable extent in dilute solution, so there is a general balance with most of the material in the form of the four ions.

Type (2) is illustrated by a mixture of solutions of silver nitrate and potassium chloride:

$$\begin{array}{lcccc} \mathrm{AgNO_3} & \leftrightarrows & \overset{+}{\mathrm{Ag}} & + & \overset{-}{\mathrm{NO_3}} \\ \mathrm{KCl} & \leftrightarrows & \mathrm{Cl} & + & \overset{+}{\mathrm{K}} \\ & & \downarrow\uparrow & & \downarrow\uparrow \\ & & \mathit{AgCl} & & \mathrm{KNO_3}. \end{array}$$

Since silver chloride is insoluble both the silver ions and chloride ions are largely removed from solution and tied up in molecules of silver chloride. This steadily aids the ionization of silver nitrate by disturbing the equilibrium to the right. All the silver nitrate ionizes. Similarly with the potassium chloride. Nothing is left but the precipitate and the ions from potassium nitrate (with a few molecules).

Exercise 2. — By this method write the equilibria in a mixture of barium chloride and sodium sulfate.

Type (3) is well represented by neutralization of an acid by a base. Here the hydroxyl and hydrogen ions are tied up in molecules of water, which ionize only to a trifling extent. Equilibria are disturbed to the right and all the acid and base used up.

$$\begin{array}{lcccc} \mathrm{NaOH} & \leftrightarrows & \overset{+}{\mathrm{Na}} & + & \overset{-}{\mathrm{OH}} \\ \mathrm{HCl} & \leftrightarrows & \overset{-}{\mathrm{Cl}} & + & \overset{+}{\mathrm{H}} \\ & & \downarrow\uparrow & & \downarrow \\ & & \mathrm{NaCl} & & \mathrm{H_2O} \end{array}$$

Neutralization.[1] — When a liter of a normal solution of *any acid* neutralizes a liter of a normal solution of *any base* 13,700 calories of heat are released. Remember, these electrolytes are ionized before mixing.

$$\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{OH}}+\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{Cl}}\rightarrow\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{Cl}}+\mathrm{H_2O}+13{,}700\text{ cal.}$$

$$\overset{+}{\mathrm{K}}+\overset{-}{\mathrm{OH}}+\overset{+}{\mathrm{H}}+\overset{-}{\mathrm{Cl}}\rightarrow\overset{+}{\mathrm{K}}+\overset{-}{\mathrm{Cl}}+\mathrm{H_2O}+13{,}700\text{ cal.}$$

$$2\ \overset{+}{\mathrm{Na}}+2\ \overset{-}{\mathrm{OH}}+2\ \overset{+}{\mathrm{H}}+\overset{--}{\mathrm{SO_4}}\rightarrow 2\ \overset{+}{\mathrm{Na}}+2\ \overset{-}{\mathrm{Cl}}+2\ \mathrm{H_2O}+27{,}400\text{ cal.}$$

$$\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{OH}}+\overset{+}{\mathrm{H}}+\mathrm{NO_3}\rightarrow\overset{+}{\mathrm{Na}}+\overset{-}{\mathrm{NO_3}}+\mathrm{H_2O}+13{,}700\text{ cal.}$$

$$\overset{++}{\mathrm{Ba}}+2\ \overset{-}{\mathrm{OH}}+2\ \overset{+}{\mathrm{H}}+2\ \overset{-}{\mathrm{Cl}}\rightarrow\overset{++}{\mathrm{Ba}}+2\ \overset{-}{\mathrm{Cl}}+2\ \mathrm{H_2O}+27{,}400\text{ cal.}$$

The only thing common to all these reactions is the formation of water. The heat of neutralization is really the heat of formation of 18 g. of water in each case. If sodium chloride really formed and stayed formed in the first reaction above, its heat of formation would be added to 13,700 cal. The same is true for the other salts mentioned, each with a different heat of formation. But the constant value of the heat of neutralization is convincing evidence that the only ions that stay together to any extent are hydrogen and hydroxyl in the form of water. So the essential feature of neutralization is the union of the hydrogen ion of an acid with the hydroxyl ion of a base to form water. Nothing else happens.

If in a conductivity apparatus such as Fig. 44 equal layers of 0.1 N HCl and 0.1 N NaOH be placed with negligible mixing, the lamp glows brightly. No wonder with the fastest ions known, $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{OH}}$, to carry most of the current. The slower $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{Cl}}$ also help. On stirring the two layers the swift $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{OH}}$ meet, neutralize each other and are removed from solution. The slower $\overset{+}{\mathrm{Na}}$ and $\overset{-}{\mathrm{Cl}}$ are all that are left to carry the current. It might be expected that since half the ions are gone only half as much current could be carried, but it is worse than that. $\overset{+}{\mathrm{H}}$ and $\overset{-}{\mathrm{OH}}$ carried more than half the current because of their greater velocity.

---

[1] In a normal solution of sodium chloride there are some un-ionized molecules, so the heat liberated must be somewhat more than 13,700 cal.

Titration with Standard Solutions. — A solution of any definite, known concentration is often called a *standard solution.* A normal solution of any acid is such a standard solution and contains 1.008 g. of ionizable hydrogen per liter. Since a normal solution of any base contains 17.008 g. ionizable hydroxyl per liter, it is evident that a liter of one exactly neutralizes a liter of the other:

$$\overset{+}{\mathrm{H}}\ (1.008\ \mathrm{g.}) + \overset{-}{\mathrm{OH}}\ (17.008\ \mathrm{g.}) \rightarrow \mathrm{H_2O}\ (18.016\ \mathrm{g.}).$$

In fact equal volumes are equivalent; so if we wished to determine the strength of an unknown solution of sodium hydroxide (or any base) and had, for example, a 0.1 N solution of hydrochloric acid, we could do this by titration. With an accurately marked pipette or burette (Fig. 45) we measure out a convenient volume, say 20 cc., of the acid into a small beaker. A few drops of litmus solution are added to this, turning red, of course. Then we carefully run in (drops, not a stream) the unknown base until one more drop just turns the red to blue. This means that there is just enough base to react exactly with the acid. Suppose 20 cc. of 0.1 N HCl neutralized 16 cc. of unknown sodium hydroxide. It is evident that the volumes of acid and base used must be inversely proportional to their normality. For example, 100 cc. of N acid would neutralize 50 cc. of

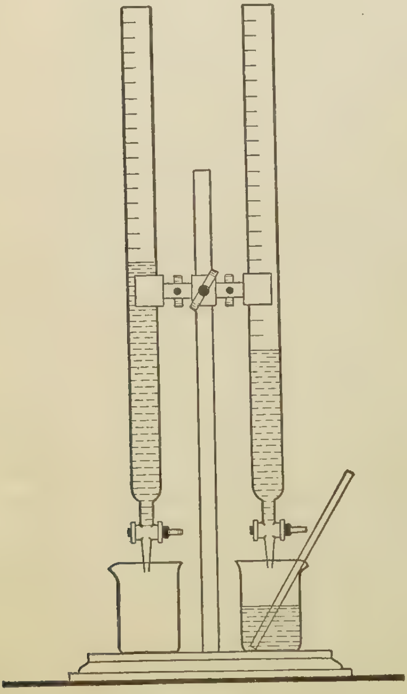


Fig. 45

2 N base. In this particular case the proportion may be expressed as follows:

$$\begin{array}{ccccccc} \text{cc. acid} & & \text{cc. base} & & \text{normality} & & \text{normality} \\ 20 & : & 16 & = & x & : & 0.1 \\ & & 16x & = & 2.0 & & \\ & & x & = & 0.125 & & \end{array}$$

Therefore the base is 0.125 N.

Such analysis of acid or base solutions is called ***acidimetry*** or ***alkalimetry.*** The color change at neutrality is called the *end-point* and the process is ***titration.***

Exercise 3. — How many cc. of 0.1 N HCl are required to neutralize 80 cc. of 0.5 N KOH?

Exercise 4. — If 44 cc. of unknown sulfuric acid neutralize 30 cc. of N KOH, how many grams of acid are contained in 1000 cc.? What is its normality?

Exercise 5. — Remembering that ammonium hydroxide in 0.1 N concentration is only 1.3 per cent ionized, while 0.1 N nitric acid is 93 per cent ionized, would you say that a liter of 0.1 N NH_4OH would just exactly be neutralized by a liter of 0.1 N HNO_3? Explain.

Indicators.[1] — Indicators are substances that change color when solutions pass from the acidic to the basic condition or vice versa. Litmus changes from red in acid to blue in base; phenolphthalein from colorless in acid to purple in base; methyl orange from pink in acid to yellow in base. The sharp color change should indicate neutrality, when the number of $\overset{+}{H}$ ions exactly equals the number of OH ions, but some indicators do not change color until there is a considerable excess of either $\overset{+}{H}$ ions or $\overset{-}{OH}$ ions. For example, there must be eighty times as many $\overset{-}{OH}$ ions as $\overset{-}{H}$ ions before phenolphthalein changes to purple. Methyl orange does not become an unmistakable pink until there are a million times as many $\overset{+}{H}$ ions as $\overset{-}{OH}$ ions. Litmus is more accurate than either. But, as McCoy and Terry put it, it is fortunate that we have indicators of various degrees of accuracy. If we titrate vinegar (for its acetic acid) with 0.1 N NaOH, we should not expect to secure exact neutrality, for the product, sodium acetate, hydrolyzes in water to form a slightly basic solution. So if we mix theoretically equal amounts of acetic acid and sodium hydroxide we must use an indicator not too sensitive to a slight excess of OH ions if the indicator is to give a useful color change. Phenolphthalein (generally used in titrating rather weak acids) is just right for this purpose.

---

[1] As an aid to a clear understanding of this topic read "Equilibrium in Acidic and Basic Solution," page 422.

It is interesting to know that thousands of indicators may be extracted from plants. As a child you removed elderberry stains with the acid of tomatoes and sometimes tried soap. You may recall the color changes. Coffee is a good indicator, as is the extract of red cabbage and an alcoholic extract of the red skin of radishes.

Hydrolysis. — Double decomposition in which water reacts with a salt to form an excess of free acid or free base is hydrolysis. Water solutions of sodium carbonate are basic. The minute ionization of water is a vital factor:

$$\begin{array}{rcl}
\mathrm{Na_2CO_3} & \leftrightarrows & 2\,\overset{+}{\mathrm{Na}} + \overset{--}{\mathrm{CO_3}} \\
2\,\mathrm{H_2O} & \leftrightarrows & 2\,\overset{-}{\mathrm{OH}} + 2\,\overset{+}{\mathrm{H}} \\
 & & \qquad \downarrow\!\uparrow \qquad\quad \downarrow \\
 & & 2\,\mathrm{NaOH}\;\; \mathrm{H_2CO_3}
\end{array}$$

Only one water molecule out of many millions is ionized, but as the few H ions are tied up in molecules of the very weak carbonic acid (H_2CO_3), every equilibrium is disturbed continuously. Of course formation of the strongly ionized sodium hydroxide does not tie up the $\overset{-}{OH}$ ions. More water ionizes and the excess of free $\overset{-}{OH}$ ions increases until the solution is very strongly alkaline. In reality the carbonic acid ionizes to a greater degree than will account for all this effect:

$$\mathrm{H_2CO_3} \leftrightarrows \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{HCO_3}}.$$

But the ion, $\overset{-}{HCO_3}$, is ionized into $\overset{+}{H}$ ion and $\overset{--}{CO_3}$ ion to such an extremely minute degree that it very effectually removes $\overset{+}{H}$ ions from the solution.

Solutions of ferric chloride react acidic:

$$FeCl_3 \leftrightarrows \overset{+++}{Fe} + 3\,\overset{-}{Cl}$$

$$\begin{array}{rccc} 3\,H_2O \leftrightarrows & 3\,\overset{-}{OH} & + & 3\,\overset{+}{H} \\ & \downarrow\uparrow & & \downarrow\uparrow \\ & Fe(OH)_3 & & 3\,HCl \end{array}$$

Ferric hydroxide is insoluble, so it removes OH ions from solution and continuously disturbs the ionization equilibrium of water. The other product, hydrochloric acid, ionizes freely and does not remove H ions. So a distinct excess of H ions develops.

Solutions of sodium chloride are neutral, as neither $\overset{+}{H}$ ions nor $\overset{-}{OH}$ ions are removed from solution:

$$NaCl \leftrightarrows \overset{+}{Na} + \overset{-}{Cl}$$

$$\begin{array}{rccc} H_2O \leftrightarrows & \overset{-}{OH} & + & \overset{+}{H} \\ & \downarrow\uparrow & & \downarrow\uparrow \\ & NaOH & & HCl \end{array}$$

Both products, sodium hydroxides and hydrochloric acid, ionize freely. There is, then, no excess of either $\overset{+}{H}$ ion or $\overset{-}{OH}$ ion.

From these type reactions we learn that a salt of a strong base and a weak acid ($2\,NaOH + H_2CO_3 \rightarrow Na_2CO_3 + H_2O$) is hydrolyzed to a basic solution. Salts of a weak base and a strong acid ($Fe(OH)_3 + 3\,HCl \rightarrow FeCl_3 + 3\,H_2O$) react acidic in water. Salts of a strong acid and a strong base ($HCl + NaOH \rightarrow NaCl + H_2O$) react neutral in water. The greater the difference in strength of the acid and base forming a salt the more the salt is hydrolyzed.

EXERCISE 6. — Diagram the hydrolysis of potassium acetate. Of sodium sulfate.

The Electromotive or Displacement Series. — We have already studied the order or activity of metals. Since taking up our study of ionization we see a new meaning in the series. A strip of zinc in dilute sulfuric acid displaces hydrogen. But a strip of zinc in a solution of copper sulfate displaces metallic copper in a manner quite similar except that molecular hydrogen escapes as a gas, while molecular copper deposits as a red powder:

$$\mathrm{Zn}+\overset{+}{\mathrm{H}}+\overset{+}{\mathrm{H}}+\overset{--}{\mathrm{SO_4}} \rightarrow \mathrm{H_2}+\overset{++}{\mathrm{Zn}}+\overset{--}{\mathrm{SO_4}},$$

$$\mathrm{Zn}+\overset{++}{\mathrm{Cu}}+\overset{--}{\mathrm{SO_4}} \rightarrow \mathrm{Cu}+\overset{++}{\mathrm{Zn}}+\overset{--}{\mathrm{SO_4}}.$$

What really happens is that the zinc atom gives two electrons to two hydrogen ions and thus becomes the positive zinc ion. Hydrogen ions with addition of electrons become neutral atoms. They cannot continue an independent existence, so they escape from solution as ordinary hydrogen (H_2). Similarly the zinc atom gives two electrons to the copper ion which without its charge is no longer blue and soluble but red and insoluble. The solution itself changes from a blue solution of copper sulfate to a colorless solution of zinc sulfate. Evidently the zinc atom is better able to throw off electrons than is hydrogen or copper. The whole electromotive series really lists the elements in the order of their ability to take on ionic charges (thus going into solution).

Now it is clear why absolutely anhydrous metallic sodium does not react with 100 per cent sulfuric acid. Without water there are no hydrogen ions to rob of their charges.

Exercise 7. — What is the result of mixing copper with a solution of zinc sulfate? Explain. Explain the action of iron on a solution of copper sulfate.

CHAPTER XIV

SULFUR AND HYDROGEN SULFIDE. CRYSTAL SYSTEMS

Sulfur was known to the ancients. The brimstone of the Bible was sulfur. Later the alchemists considered it one of the three fundamental elements.

Occurrence. — Sulfur occurs free in volcanic regions, possibly because of the reaction between sulfur dioxide and hydrogen sulfide found in volcanic gases:

$$2\ H_2S + SO_2 \rightarrow 2\ H_2O + 3\ S.$$

Sedimentary sulfur also occurs in large deposits because of the reduction of calcium sulfate by bituminous material to form calcium sulfide (CaS), the release of hydrogen sulfide by the action of carbonic acid on the calcium sulfide and final oxidation of the hydrogen sulfide to free sulfur. Up to 1900 Sicily produced 90 per cent of the world's sulfur, but for several years its production has declined. About 1904 the production of Louisiana sulfur by the Frasch process made the United States quite independent. Previously we imported about 175,000 tons annually. This country probably led the world in sulfur production during the Great War, but in peace the domestic market will not warrant such great production. Spain, Mexico, Japan, Greece, Iceland and other countries produce sulfur, but not in quantities comparable to the output of the United States and Italy.

Combined sulfur is very common. Iron pyrites (FeS_2), once called "fool's gold," is found in most of our states and in nearly all countries. In fact some of our most important metals occur combined with sulfur, as lead sulfide or galena (PbS), zinc blende (ZnS), and chalcopyrite ($CuFeS_2$). The sulfates also occur in great quantities. The most common are calcium sulfate or gypsum ($CaSO_4.2\ H_2O$), barite ($BaSO_4$), celestite ($SrSO_4$) and Epsom salt ($MgSO_4.7\ H_2O$).

Sulfur is an essential element in all protein material and so is found combined in plants and animals. Hence the production of the offensive smelling hydrogen sulfide on decay. Egg yolk is so rich in combined sulfur that antique eggs are easily recognized by the overpowering odor of hydrogen sulfide.

Preparation. — In Sicily sulfur occurs mixed with much rock. The mixture is piled up on a hillside, covered with earth and, by burning a small amount of the sulfur at properly regulated draft holes, the rest is melted away from the rocks and dirt. It melts at 114.5°, so this is easily done. Formerly one third of the sulfur was lost as fuel, but this has been reduced by modern economies in heat saving. Italy has no coal, so it is cheaper to heat with sulfur. To further purify the crude sulfur which was run off from these kilns it is heated in iron retorts. Sulfur volatilizes at very moderate temperatures and thus is distilled away from its impurities. The vapors are condensed in large brick chambers. At first before the brick walls are heated by the gases, the sulfur settles as a yellow dust called "flowers of sulfur." Later it condenses as a liquid which is cast into sticks of "roll sulfur."

In the United States the clever invention of Herman Frasch, an American chemist, made possible the cheapest production of pure sulfur (99.5 per cent) yet known. In Louisiana and Texas great beds of sulfur occur at depths approaching 900 ft. Borings through the overlying rock reach the bottom of these deposits and through this hole four concentric pipes are driven (Fig. 46). The outer pipe has a diameter of about 8 cm. (3 in.). Relying on the remarkably low melting point of sulfur (114.5°) water at 170° C. under 100 lbs. pressure is forced down an outer pipe to melt the sulfur. But sulfur is twice as heavy as water, so to make it lighter hot air is forced down the

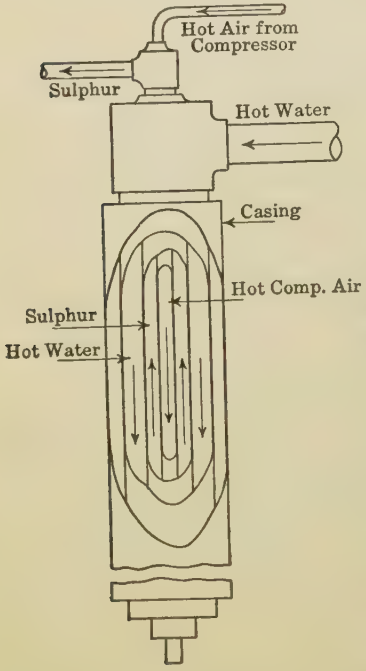


Fig. 46

innermost pipe (1 in.) to fill the liquid with bubbles. The frothy mixture rises between the air pipe and the hot water pipe and flows into great wooden bins, where it cools to huge blocks. Many wells yield 500 tons daily. Some of the bins are 60×150×250 ft. and produce a single block containing 100,000 tons of sulfur. The great block is dynamited into fragments, as needed for loading on trains.

Before the Great War the United States produced nearly 275,000 tons of sulfur annually, exporting more than we imported. During the conflict, ships were needed so desperately for troop and supply transportation that we could no longer import Spanish pyrites for the manufacture of the sulfuric acid so vital to munition production. It was then that this brilliant American achievement in sulfur mining saved the day. Production in Louisiana and Texas was forced to a figure not officially announced, but said to be about 1,000,000 tons per year. Special burners were made so this sulfur could be burned into sulfur dioxide and thus changed into sulfuric acid. Such a huge production (more than the whole world needed ten years ago) will not find an adequate market now, so it is probable that production will remain near 300,000 tons.

A little sulfur has been recovered by the Chance process from the waste calcium sulfide of the Le Blanc soda manufacture. Some is also made by heating pyrites to 900° with a reducing flame. As a result of a number of reactions all the sulfur in the pyrites is obtained. It is now proposed that the waste sulfur dioxide from Western smelters be treated with steam and a reducing flame to secure the sulfur.

Exercise 1. — Why doesn't the dirt come up with the melted sulfur in the Frasch process?

Physical Properties. — Sulfur is a pale-yellow solid, tasteless, and nearly odorless, insoluble in water but soluble in carbon disulfide and some other solvents. It exists in a number of different forms with distinctly different properties. This is an example of *allotropy*. Ozone and ordinary oxygen are allotropic forms of the same element. White and red phosphorus are also examples of allotropes. The stable form of sulfur, at ordinary temperatures, crystallizes in the rhombic system, but above 96° it slowly changes into the needle-like monoclinic crystals. On cooling the monoclinic crystals below 96° they change very slowly to rhombic crystals. Thus 96° is a transition point.

Exercise 2. — In what connection have we mentioned transition points before?

There is a distinct change in properties in this transition. The density of rhombic sulfur is 2.06 and its melting point 114.5°. The density of monoclinic sulfur is 1.96 and its melting point 119.° Of course natural sulfur is rhombic. This form can be obtained in the laboratory by allowing a solution in carbon disulfide to evaporate slowly (away from flames). If a large mass of molten sulfur (about 200 g.) be cooled slowly, the surface crust punctured and the liquid below poured out, the dish will be found to contain a mass of needles of monoclinic sulfur. On long standing below 96° these become rhombic. Apparently the needles remain, but upon examination they are found to be made up of minute rhombic crystals.

Crystal Systems. — When a liquid solidifies it is usually found to be made up of particles of regular geometric form called crystals. Crystals are also formed by evaporation of solutions and cooling of some vapors. Crystals often mass together so as to make their individual forms indistinct, that is, we have a crystalline mass. Perfect crystals have plane surfaces meeting at definite angles and their edges are straight lines. There are so many different shapes known that the subject of crystallography may seem hopeless. However, these plane surfaces are arranged with reference to imaginary lines, called axes of symmetry, drawn through the crystal. There are only six arrangements of these axes, so there are only six crystal systems.

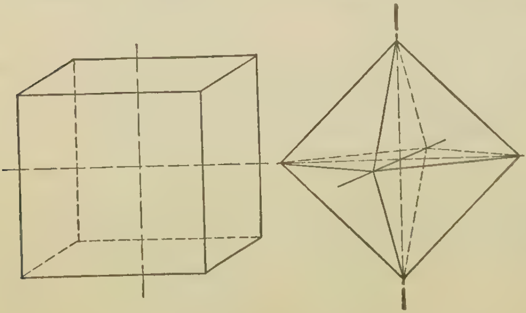


Fig. 47

1. Isometric or cubic system: three axes of equal length at right angles to each other (Fig. 47). Examples, alum and sodium chloride.

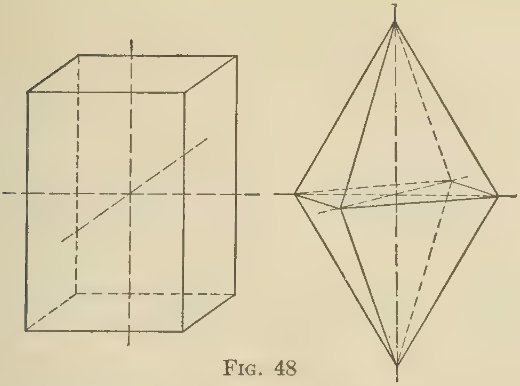


FIG. 48

2. Tetragonal system: two equal axes and one of different length, all at right angles to each other (Fig. 48). Example, nickel sulfate.

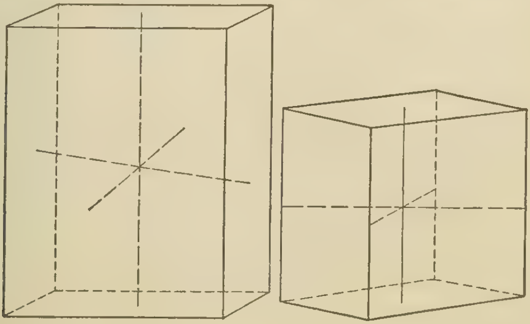


FIG. 49

3. Rhombic system: three unequal axes, all at right angles (Fig. 49). Examples, sulfur and potassium nitrate.

4. Monoclinic system: two axes at right angles and a third at right angles to one but inclined with reference to the other. The axes may vary in relative lengths (Fig. 50). Examples, gypsum and sodium carbonate.

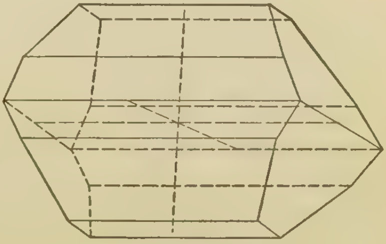


FIG. 50

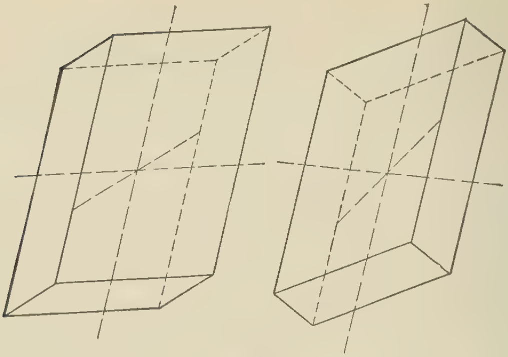


FIG. 51

5. Triclinic system: three axes, all inclined toward each other and of any relative lengths or inclinations (Fig. 51).

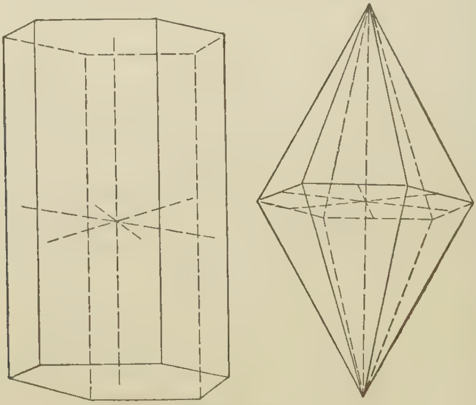


FIG. 52

6. Hexagonal system: three equal axes in the same plane intersecting at angles of 60° and a fourth at right angles to all of these (Fig. 52). Example, quartz.

Crystals of widely different shapes may belong to the same system as indicated by the angles between their axes and by their relative lengths. For example, the four crystals of Fig. 53 all belong to the cubic system.

Recent X-ray studies indicate that in crystals the atoms are arranged in an orderly pattern so that molecular grouping no

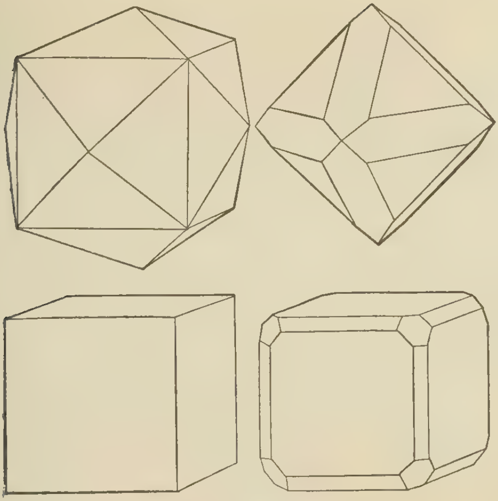


FIG. 53

longer exists. The properties of crystals differ when measured in different directions and they split in definite planes. Diamonds are crystalline, but the facets are cut to suit the lapidary and not in agreement with the natural form of that crystal. Sulfur as we learned has two crystal forms, and an energy change is involved in a change from one to the other. When a substance crystallizes in two systems it is *dimorphous* and two or more substances crystallizing in the same form are *isomorphous*. The crystal form is a valuable aid in the identification of substances. Liquids may be cooled too rapidly to permit crystallization and in such cases glassy or gummy substances result.

EXERCISE 3. — Concentrate some salt water and let it stand undisturbed in an open dish. To what system do these crystals belong? Examine good crystals of quartz, calcium carbonate, cane sugar (as seen in some fruit jellies or in rock candy) and copper sulfate, and name their crystal system.

Amorphous Sulfur. — When sulfur is melted at 114.5° it is a pale-yellow, mobile liquid. At 160° it darkens and becomes very viscous. At 180° the tube can be inverted and the sulfur does not run out. Above this temperature the sulfur again becomes more fluid and boils at 444.7°. Alexander Smith calls the pale yellow liquid $S\lambda$ and the thick dark liquid $S\mu$. He proved that at intermediate temperatures the two forms are in equilibrium, shifting with the temperature. If sulfur heated nearly to boiling be quickly poured into cold water, it solidifies before crystals have time to form and is a rubbery mass. This soon hardens and then is only partially soluble in carbon disulfide. Crystalline S is removed by this solvent, leaving noncrystalline $S\mu$.

Amorphous $S\mu$ is also made by the reaction between sulfur dioxide and hydrogen sulfide, at 0°. (See page 174.) Solutions of polysulfides when acidified yield a suspension of $S\mu$ called *milk of sulfur*. The solid removed after slow settling is insoluble in carbon disulfide.

Sulfur Vapor. — At 250° (under low pressure) sulfur must be represented by S_8 since 22.4 liters weigh 256 g. At 800° the G. M.V. weighs 64 g., so S_2 is then the formula. At intermediate temperatures S_6 may exist but probably only mixtures of S_8 and S_2. At 2000° the element is monatomic and S_1 is the formula.

Chemical Properties. — Sulfur is very active when heated. Merely rubbing it in a mortar with mercury produces black mercuric sulfide (HgS). When heated it unites with all metals except gold and platinum and, when once started, much heat is evolved. If a tube of sulfur and iron filings be heated to glowing, the glowing continues even after removal from the flame. Moist sulfur is slowly oxidized in the air:

$$2\,S + 2\,H_2O + 3\,O_2 \rightarrow 2\,H_2SO_4.$$

It can be oxidized quickly by strong oxidizing agents such as hot nitric acid. In fact sulfur compounds are torn down by this method and the sulfur converted into sulfuric acid. It may then be converted into insoluble barium sulfate and weighed. This is the basis of our quantitative determination of sulfur in minerals, and in foods. Of course hot sulfur burns in air to form sulfur dioxide — and a trace of trioxide.

Hot sulfur unites with carbon to form carbon disulfide, with hydrogen to form hydrogen sulfide and with chlorine to form sulfur monochloride (S_2Cl_2). This was once thought to be SCl, hence the misleading name. Here the valence of sulfur is one, but in H_2S it is two, in SO_2 it is four and in SO_3 it is six.

Uses. — In 1917 the United States used 500,000 tons of sulfur in the manufacture of sulfuric acid, but in peace times the largest use is in making sulfite for paper pulp. In 1914 we diverted 136,000 tons for that purpose. Large quantities are needed for vulcanizing rubber. Raw rubber is too hard in winter and too sticky in summer for practical use, but when heated with sulfur it becomes stronger, more elastic and is far less affected by temperature changes. Sulfur may be applied directly or dissolved in sulfur monochloride or as antimony sulfide (in red rubber). Sulfur is used in making sulfur monochloride, which has another outlet besides the rubber industry. It is the foundation of mustard gas, the most effective poison gas of the war. Sulfur is in demand in the manufacture of carbon disulfide and matches and the sulfur black dyes. Free sulfur is a necessary part of black gunpowder and of many fungicides and germicides for plants. Europe applies 100,000 tons of the element to vines and hops annually. The lime-sulfur spray is famous in this country. As a basis for sulfur dioxide it is necessary in bleaching straw and some other fabrics and has been in demand for bleaching dried fruits, English walnuts, etc.

It is interesting to connect this common element with the Great War. Necessary to the production of mustard gas, necessary to the production of rubber for tires, masks, balloons, and surgical supplies, and necessary to the manufacture of sulfuric acid, itself the foundation of most chemical industries — sulfur played a prominent military part.

Exercise 4. — How many grams of sulfur are required to make 45 liters of sulfur dioxide?

HYDROGEN SULFIDE

Scheele (1777) published the first detailed investigation of its properties, although something was known of hydrogen sulfide before his time. Soon after this it was used in analysis. At the very time that Lavoisier was insisting that all acids contained oxygen it was shown that hydrogen sulfide is not an oxygen acid.

Exercise 5. — How did Lavoisier reconcile the composition of hydrochloric acid with his views on acids?

Hydrogen sulfide is found in some natural waters, such as the so-called "sulfur springs" and in volcanic gases. Since albuminous material contains combined sulfur, its decay in the absence of air produces hydrogen sulfide. Thus sewer gas always contains hydrogen sulfide.

Preparation. — Hydrogen unites with hot sulfur vapor to form hydrogen sulfide. The most convenient laboratory method of preparation is the addition of some nonoxidizing acid to a sulfide, preferably ferrous sulfide (FeS) because it is the cheapest:

$$FeS + 2\,HCl \rightarrow FeCl_2 + H_2S$$

This reaction is reversed very slightly, partly because the gas is only moderately soluble and most of it escapes. It might reasonably be expected that iron pyrites (FeS_2) would be better since it is still cheaper but is not used because it does not react with an acid to form hydrogen sulfide, unless nascent hydrogen is present.

Soluble sulfides such as sodium sulfide react with acid more rapidly (better contact), but for simple regulation of flow as in a Kipp generator the insoluble ferrous sulfide is best:

$$Na_2S + 2\,HCl \rightarrow 2\,NaCl + H_2S.$$

Since hydrogen sulfide is an acid in aqueous solution, the sulfides of metals are its salts. Many occur in nature and many are formed by addition of soluble sulfides to salt solutions. Any sulfate can be reduced by heating with carbon. Hydrogen sulfide can be made from the resulting metallic sulfide. In this way a sulfate can be recognized and decomposed for analysis:

$$BaSO_4 + 2\,C \rightarrow BaS + 2\,CO_2,$$
$$BaS + 2\,HCl \rightarrow BaCl_2 + H_2S.$$

Physical Properties. — Hydrogen sulfide is a colorless gas, liquefying at −60° and freezing at −83°. Its critical temperature is 100°. At room temperatures about three volumes dissolve in one volume of water. It readily escapes from water. The odor is disgusting. Small amounts in the air may cause headaches and nausea. Air containing 1 part in 200 is fatal if breathed long and the concentrated gas is quickly fatal. The gas is about one and a fifth times as heavy as air, so it can be collected by air displacement. (Why not over water?)

Chemical Properties. — A solution of hydrogen sulfide open to the air soon has a film of sulfur on the surface, showing how easily it is oxidized. A rapid oxidation is secured by burning the gas in air:

$$2\ H_2S + O_2 \rightarrow 2\ H_2O + 2\ S.$$

If a cold dish be held in the middle of the burning jet for a minute a yellow spot forms. This is sulfur, of course, and shows that in the interior of the flame where there is no contact with air the unburned gas has been dissociated by heat. The dish merely condenses the sulfur vapor before it has opportunity to burn (Fig. 54):

$$H_2S \leftrightarrows H_2 + S.$$

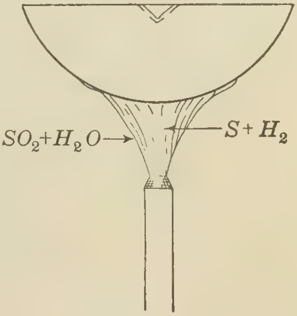


FIG. 54

EXERCISE 6. — What are the products when hydrogen sulfide is burned with a large supply of air?

This reaction is reversible, as the two elements are known to unite when heated. The gas cannot be dried by concentrated sulfuric acid because the concentrated acid oxidizes it. Phosphorus pentoxide is a suitable dryer in this case. Oxidizing agents of all kinds attack hydrogen sulfide.

On one occasion the author asked an assistant to fill a Kipp generator with ferrous sulfide and hydrochloric acid. Failure to get any hydrogen sulfide forced an investigation. A red-brown gas was observed along with a yellow-white precipitate. It was evident at once that the assistant had used nitric acid by mistake, for although this reacted to form hydrogen sulfide, the nitric acid promptly oxidized the gas into sulfur. The red-brown gas was an oxide of nitrogen left over as a fragment of the nitric acid after it gave up oxygen:

$$2\ H_2S + 2\ HNO_3 \rightarrow 4\ H_2O + 2\ NO + 3\ S,$$
$$2\ NO + O_2 \text{ (from air)} \rightarrow 2\ NO_2 \text{ red-brown.}$$

As an oxidizing agent dilute nitric acid yields three oxygen atoms for every two molecules. Potassium permanganate and dichromate readily oxidize hydrogen sulfide, releasing free sulfur. When the student later uses this gas in qualitative analysis he must expect this free sulfur if any oxidizing agent be present. Even ferric chloride is reduced by it to ferrous chloride:

$$2\ FeCl_3 + H_2S \rightarrow 2\ FeCl_2 + 2\ HCl + S,$$

Hydrogen sulfide is an extremely weak acid in water solution. The first hydrogen atom ionizes very little and the second to a minute degree, less than water, in fact:

$$H_2S \leftrightarrows \overset{+}{H} + \overset{-}{HS},$$

$$\overset{-}{HS} \leftrightarrows \overset{+}{H} + \overset{--}{S}.$$

Use in Analysis. — Hydrogen sulfide is invaluable in qualitative analysis and useful in quantitative work also. In a solution of copper sulfate, for example, this gas precipitates black cupric sulfide:

$$CuSO_4 + H_2S \rightarrow CuS + H_2SO_4$$

Other sulfides formed in similar ways are black HgS, orange Sb_2S_3, yellow As_2S_3 and CdS, and white ZnS. In the system of qualitative analysis we divide the sulfides into two great groups.

1. Sulfides insoluble in dilute acid (CuS, HgS, As_2S_3, etc.).
2. Sulfides insoluble in neutral or alkaline solution but soluble in dilute acid (NiS, MnS, ZnS, etc.).

The reason zinc sulfide, for example, is not precipitated in acid solution is that addition of a strong acid like hydrochloric increases greatly the number of $\overset{+}{H}$ ions present. This gives infinitely more opportunities for contact between the very few $\overset{--}{S}$ ions and $\overset{+}{H}$ ions so more $\overset{--}{S}$ ions are removed from the field, tied up as $\overset{-}{HS}$ ions or H_2S molecules. This leaves so few $\overset{--}{S}$ ions that the $\overset{++}{Zn}$ ions do not form enough zinc sulfide molecules to saturate the solution and thus precipitate.

How different if a strong base be added! The great excess of $\overset{-}{OH}$ ions ties up nearly all the $\overset{+}{H}$ ions and so the equilibrium is disturbed to the right, producing an enormous increase in number of $\overset{--}{S}$ ions.

$$H_2S \leftrightarrows \overset{+}{H} + \overset{+}{H} + \overset{--}{S}$$

Now there are enough of $\overset{--}{S}$ to react with $\overset{++}{Zn}$ ions and form more zinc sulfide than the solution will hold. Precipitation occurs.

The sulfides of copper and its group are so much more insoluble in water that they can be precipitated in spite of suppression of ionization of hydrogen sulfide by any strong acid. Ferrous sulfide is so susceptible to the action of acid that it cannot be precipitated by passing hydrogen sulfide into a ferrous salt:

$$FeCl_2 + H_2S \leftrightarrows FeS + 2\ HCl.$$

This equilibrium puts nearly everything on the left. The hydrochloric acid formed may be said to dissolve the sulfide. It really suppresses the ionization of the hydrogen sulfide. But add a base. The acid is neutralized and ferrous sulfide precipitates at once.

There are a few sulfides which are hydrolyzed completely in water, so attempts to precipitate them (in absence of acid) produce hydroxides:

$$Al_2S_3 + 6\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2S.$$

Sodium, potassium and ammonium sulfides are soluble and are hydrolyzed considerably.

Exercise 7. — How does hydrogen sulfide react with iodine?

Exercise 8. — Since sodium sulfide (Na_2S) is a salt of $NaOH + H_2S$, represent graphically its hydrolysis in solution.

When an *excess* of hydrogen sulfide is passed into sodium hydroxide solution, for example, only NaHS is produced. To make Na_2S, an equivalent quantity of sodium hydroxide must be added:

$$NaOH + NaHS \rightarrow Na_2S + H_2O.$$

This is accomplished quite simply by dividing any solution of the base into two equal parts, saturating one part and then mixing the two parts.

Exercise 9. — Does this suggest a convenient way to make Na_2SO_3 instead of $NaHSO_3$ from SO_2? Or Na_2CO_3 from CO_2? These three gases have a certain resemblance.

Polysulfides. — When sulfur is shaken or warmed with a solution of a sulfide, a polysulfide is formed:

$$Na_2S + S \rightarrow Na_2S_2.$$

Evaporation produces residues corresponding to formulas ranging from Na_2S_2 to Na_2S_5, depending upon how much sulfur was added. All the persulfides (polysulfides) are unstable, slowly releasing sulfur. This makes them invaluable as insecticides and fungicides.

Lime-sulfur wash (CaS_4 or CaS_5) is a famous one. Yellow ammonium sulfide, $(NH_4)_2S_x$, is a reagent in qualitative analysis and is more red than yellow to tell the truth. The bottle labeled $(NH_4)_2S$ should contain a colorless liquid, but it always has a yellow tint because of decomposition with release of free sulfur which then adds on to other molecules, forming a little of the colored polysulfide.

If acid be poured into a polysulfide, free sulfur is formed and hydrogen sulfide escapes (write the equation); but if the polysulfide be poured into very dilute acid, a yellow oil separates, probably H_2S_5. (Write the equation for this.)

Exercise 10. — 100 grams of sulfur heated with copper gave 298.27 g. of copper sulfide (CuS). If you knew only that the atomic weight of sulfur was 32.06 and that the atomic weight of copper was in the neighborhood of 60–70, how would you calculate the exact atomic weight of copper?

CHAPTER XV

SULFURIC ACID AND THE OXIDES OF SULFUR

Oxides	Acids	
Sulfur dioxide (SO_2): colorless gas.	Sulfurous acid	H_2SO_3
Sulfur trioxide — (SO_3): colorless liquid.	Sulfuric acid	H_2SO_4
Sulfur "sesquioxide" (S_2O_3): blue-green solid.	Thiosulfuric acid	$H_2S_2O_3$
Sulfur hexoxide (S_2O_6): white solid	Pyrosulfuric acid	$H_2S_2O_7$
Sulfur heptoxide (S_2O_7): viscous liquid	Persulfuric acid.	$H_2S_2O_8$
	Dithionic acid	$H_2S_2O_6$
	Trithionic acid	$H_2S_3O_6$
	Tetrathionic acid	$H_2S_4O_6$
	Pentathionic acid	$H_2S_5O_6$
	Hexathionic acid	$H_2S_6O_6$

In this year's work the student will have little to do with more than the dioxide and trioxide, sulfurous, sulfuric and thiosulfuric acids.

SULFUR DIOXIDE

There is nothing new about sulfur dioxide. It was mentioned in Homer's time as a disinfectant; and Paracelsus, the alchemist, knew something of its bleaching powers. Priestley first made it in pure form and recognized it as a definite compound (1775). It occurs in volcanic gases and in some spring waters.

EXERCISE 1. — What relation has this occurrence to the great sulfur deposits in Italy? (See previous chapter.)

Preparation. — I. *Burning Sulfur.* Sulfur burns in air with a pale blue flame. Except under the pressure of war needs this is not usually considered the best source because of the cost:

$$S + O_2 \rightarrow SO_2.$$

2. ***Roasting Sulfide Ores.*** This is the cheapest commercial source of sulfur dioxide. Many common metals occur as sulfides and in roasting gases are produced which are dangerous to vegetation and to health. In some states laws forced the smelters to prevent this nuisance. As a result many smelters attached sulfuric acid plants to utilize the waste sulfur dioxide, so everybody profited. The situation is complicated if the smelter be in the Rocky Mountains, so far from sulfuric acid markets that the freight rates are prohibitive. The great copper and zinc smelter at Anaconda, Montana, solved the nuisance problem by building a giant stack over 600 feet high on a hill still higher. Consequently the fumes from the roasting sulfides are mixed with the atmosphere at a height considerably more than 1000 feet above the valley and the winds carry it away at safe dilutions. This plant utilizes some of the sulfur dioxide and may finally use it all.

The cheapest sulfide ore is iron pyrites (FeS_2), which burns like coal:

$$4\ FeS + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2.$$

Zinc sulfide (ZnS) must be fed preheated air:

$$2\ ZnS + 3\ O_2 \rightarrow 2\ ZnO + 2\ SO_2.$$

Sulfur dioxide from roasting sulfide ores is, of course, diluted with several volumes of nitrogen from the air. For this reason it is suitable only for sulfuric acid manufacture.

3. ***Reduction of Sulfuric Acid.*** Hot, concentrated sulfuric acid readily gives one oxygen from each molecule to metals and other reducing agents. In fact under some conditions it has been known to give up all of its oxygen. A very convenient laboratory method of preparation makes use of this principle. Copper scrap is heated with the concentrated acid, but is not made hot enough to boil the acid.

$$\begin{array}{ll} (1) & Cu + H_2SO_4 \rightarrow CuO + H_2O + SO_2 \\ (2) & CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O \\ \hline (3) & Cu + 2\ H_2SO_4 \rightarrow CuSO_4 + 2\ H_2O + SO_2. \end{array}$$

We remember from its place in the activity series of metals that copper does not displace hydrogen from acids, so it is clearer to write this reaction in steps. At first the copper is oxidized and then the copper oxide is readily attacked by acid. Equation (3) sums up (1) and (2).

Carbon may be used or even sulfur instead of copper:

$$C + 2\,H_2SO_4 \rightarrow CO_2 + 2\,SO_2 + 2\,H_2O.$$

Exercise 2. — Write the equation for the oxidation of sulfur by sulfuric acid.

4. *Heat Decomposition of Sulfuric Acid.* A high quality of sulfur dioxide largely used for the preparation of the sulfites used in paper making is made as follows:

$$2\,H_2SO_4 \rightarrow 2\,H_2O + O_2 + 2\,SO_2$$

Concentrated acid is dropped into a red-hot iron retort and a greater decomposition follows than is found in merely boiling the acid.

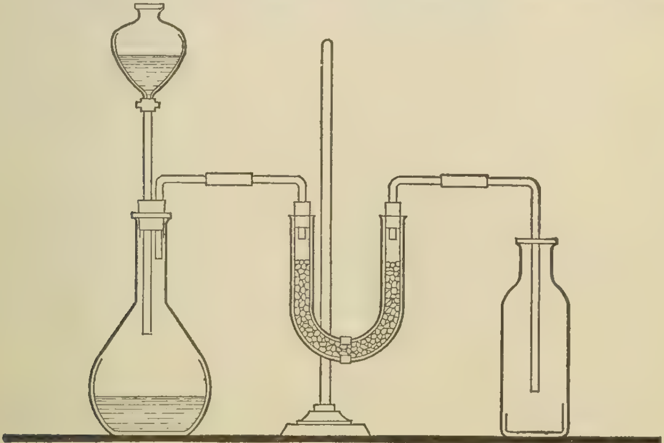


Fig. 55

5. *Acids on Sulfites.* A simple laboratory method of preparation is found in the slow dropping of some dilute acid on sulfites. The gas may be dried over anhydrous calcium chloride, as in Fig. 55:

$$Na_2SO_3 + 2\,HCl \rightarrow 2\,NaCl + H_2O + SO_2.$$

Physical Properties. — Sulfur dioxide is a colorless gas with a peculiar choking odor. It is 2.2 times as heavy as air and is easily liquefied. In fact an ice-salt mixture will liquefy it at ordinary pressures. The liquid boils at −8° and freezes at −76° into a snowlike solid. It is conveniently kept for laboratory use in tin cylinders. Fifty volumes dissolves in one volume of water at 0° and 760 mm.

Chemical Properties. — A water solution of sulfur dioxide reacts weakly acid and when bases are added sulfites are formed. This indicates a reaction with water. Sulfurous acid and sulfur dioxide are both present in equilibrium:

$$SO_2 + H_2O \leftrightarrows H_2SO_3.$$

Sulfur dioxide reacts with chlorine to form sulfuryl chloride:

$$SO_2 + Cl_2 \rightarrow SO_2Cl_2.$$

In addition to its reaction with water, with chlorine, and with hydrogen sulfide, sulfur dioxide unites with oxygen to form sulfur trioxide, a reaction greatly aided by suitable catalysts. In the presence of moisture it is a strong reducing agent and has valuable bleaching properties.

Exercise 3. — What is the reaction with hydrogen sulfide?

Uses. — Sulfur dioxide is used to some extent as a refrigerant (because it is volatilized and liquefied at convenient temperatures). Huge quantities are necessary to the manufacture of sulfuric acid and of calcium sulfite for paper making. A great deal is used in bleaching and some in fumigation, although formaldehyde has almost displaced it from that field.

Sulfurous Acid. — As stated in connection with sulfur dioxide sulfurous acid is formed to a limited extent by reaction of that gas with water. It is a weak acid ionizing in two stages:

$$(1)\ H_2SO_3 \leftrightarrows \overset{+}{H} + \overset{-}{HSO_3},$$

$$(2)\ \overset{-}{HSO_3} \leftrightarrows \overset{+}{H} + \overset{--}{SO_3}.$$

Reaction (1) proceeds to the right to a slight extent and reaction (2) to a minute extent. Addition of $\overset{-}{OH}$ ions from a strong base disturbs both these equilibria to the right.

In the air this acid adds on oxygen to form sulfuric acid and in general it acts as a strong reducing agent. A trace of sugar or glycerin greatly retards the rate of oxidation of sulfurous acid, a good example of negative catalysis. The bleaching action of sulfurous acid is probably due to combination with the color rather than reduction. Since chlorine attacks the fabrics of wool and silk, this acid, because of its gentler action, finds great use in bleaching these materials as well as paper and straw. A moist flower in a bottle of sulfur dioxide shows a marked color change.

In previous years it was the common practice to whiten canned corn and dried fruits by means of this substance, but there was some question as to the effect on health, so legal restrictions were imposed. Under Sulfur Dioxide other uses were given, since the acid is always present in moist sulfur dioxide.

Exercise 4. — To remove excess chlorine after a fabric has been bleached with that substance an "antichlor" is added. "Hypo" and sulfurous acid or sulfites are used. Write the equations showing how sulfurous acid in water uses up the free chlorine.

Sulfites. — If an excess of sulfur dioxide be bubbled through a solution of a base such as sodium hydroxide an acid salt called sodium bisulfite is formed:

$$NaOH + H_2SO_3 \rightarrow NaHSO_3 + H_2O.$$

This reminds us of the similar reaction of hydrogen sulfide. And just as with that gas, addition of an equivalent amount of the base to the solution of bisulfite forms the normal sulfite:

$$NaOH + NaHSO_3 \rightarrow Na_2SO_3 + H_2O.$$

Exercise 5. — How does this reaction prove that the $H\bar{S}O_3$ ion dissociates at least slightly into simpler ions?

Calcium bisulfite, $Ca(HSO_3)_2$, is the most important of these salts because of its ability to dissolve the lignin which cements the fibers of cellulose in wood. Chips of soft woods are heated in bisulfite solutions and the cellulose fibers are separated as paper pulp.

The normal sulfites of metals are all insoluble (except those of sodium and potassium) and the acid sulfites are all soluble. Since the sulfites slowly add on oxygen, they become contaminated in time with a little sulfate as impurity. Naturally they have reducing power.

Exercise 6. — How is calcium bisulfite made?

Sulfur Trioxide. — Sulfur trioxide is a colorless liquid boiling at 46° and freezing at 15°. It readily *polymerizes* (two or more molecules uniting to form larger molecules) especially in the presence of traces of moisture, forming sulfur hexoxide (S_2O_6), a white crystalline mass looking like asbestos. Sulfur trioxide reacts with water to form sulfuric acid. Under Sulfur Dioxide and Sulfuric Acid we discuss its formation by the catalytic oxidation of the dioxide.

Sulfuric Acid

Sulfuric acid was much used by the alchemists. Basil Valentine, in the fifteenth century, secured sulfur trioxide and the acid by distilling ferric sulfate and Geber writes of making it from other sulfates in the thirteenth century. Yet the manufacture of this great acid, the most important compound made by man, was not put on a commercial basis before 1765. Then sulfur and "niter" (KNO_3) were burned together in glass globes. In 1793 the oxidation process was made continuous by the employment of oxides of nitrogen as a catalyst.

The industry is now so enormous that the United States made over 4,000,000 tons in 1914. There are two rival processes of manufacture, each especially adapted to certain kinds of raw material and each suited to certain grades of product.

Lead Chamber Process. — The essential reactions in the huge lead-walled towers and chambers involve the oxidation of sulfur dioxide to the trioxide in the presence of enough water to form sulfuric acid. A mixture of air and the dioxide reacts very slowly, so nitric acid vapors are introduced to oxidize more rapidly:

$$2\,HNO_3 + H_2O + 2\,SO_2 \rightarrow 2\,H_2SO_4 + NO + NO_2.$$

The cost of nitric acid would make this process economically impossible were it not for the fortunate fact that the nitrogen dioxide (NO_2) released as a by-product is itself capable of oxidizing sulfur dioxide:

$$SO_2 + H_2O + NO_2 \rightarrow H_2SO_4 + NO.$$

Now another fortunate fact saves the day — and much money. If this nitric oxide (NO), the by-product here, were wasted, the lead chamber process would soon become historical only. But luckily this nitric oxide has a property — possibly somewhat dry for the student but of thrilling interest to the men owning lead chamber plants — a property of rapidly uniting with the oxygen of air to form the useful nitrogen dioxide:

$$2\,NO + O_2 \rightarrow 2\,NO_2$$

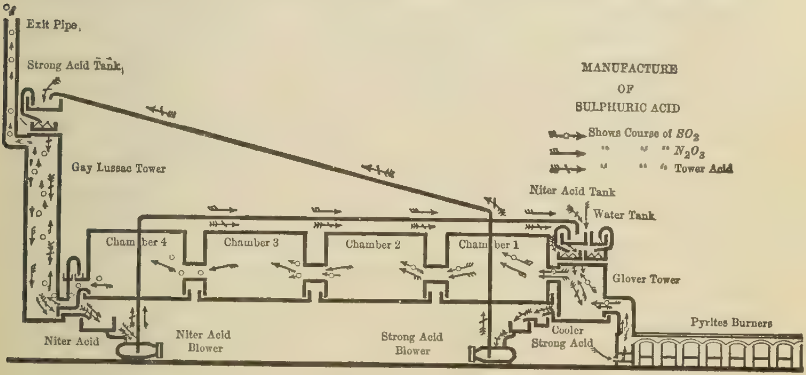


FIG. 56

In fact nitric oxide is a catalyst, making the oxygen of air unite with sulfur dioxide in a roundabout way and itself being regenerated time after time. The nitric acid, then, was merely a starter — a source of the oxides of nitrogen. Most authorities refer to nitrogen trioxide as the catalyst. However at the temperature of the lead chambers this gas dissociates to a very great extent as follows:

$$N_2O_3 \leftrightarrows NO + NO_2.$$

The explanation is quite logical for either gas as catalyst, but it is simpler as given above. There is yet much dispute about these reactions.

As shown in the diagram, Fig. 56, the sulfur dioxide is produced in the burners by roasting some sulfide, usually iron pyrites, in a strong draft of air. The pot containing sodium nitrate and concentrated sulfuric acid is heated by the flue gas to distil off nitric acid:

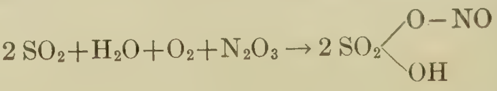
$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3.$$

This mixture of flue gases, nitrogen of air, excess oxygen, sulfur dioxide and the nitric acid vapors enter the Glover tower. This is a tall tower loosely filled with broken tile, coke or brick in order to force good mixing of the gases with the liquid splashing down from the top of the tower. This liquid supplies the water necessary, so the reactions mentioned now proceed in this tower. Possibly about 16% of the total acid of the plant is formed right in this tower.

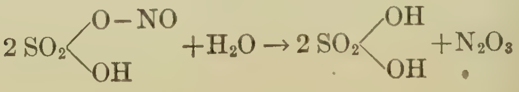
The liquid introduced at the top is a compound of oxides of nitrogen with concentrated sulfuric acid. Luckily this is decomposed by water with instant release of the oxides of nitrogen, ready for work as catalyst. So a stream of concentrated "nitrosyl" sulfuric acid meets a stream of water *inside* the tower. Here a nice economy operates. The released oxides of nitrogen (with those from the action of nitric acid) are swept on by the great stream of other gases into the first chamber. But the diluted acid splashing down the tower meets hot gases fresh from the burners, water is evaporated and passes on into the chambers as steam (where it is needed), and the acid, now cheaply concentrated, is tapped off at the base of the tower. Everything goes just where it is needed, apparently nothing wasted.

The lead chambers, from three to five in number, are huge affairs often 50 × 150 × 200 feet, each with capacities of over 150,000 cubic feet. They are really inverted boxes suspended so that their lower edges allow the constant overflow of acid collecting on the floor but do not allow escape of gases except by the stack or Gay-Lussac tower. These chambers are lined with sheets of lead melted together at the edges by oxyhydrogen flames. Lead is used because it is not attacked by acid of the concentration produced in the chambers.

The reactions already given express only the general effect of the oxides of nitrogen. It is really somewhat more complicated, and according to Lunge we must imagine the intermediate formation and decomposition of nitrosyl sulfuric acid. He uses nitrogen trioxide in his equations (at chamber temperatures largely a mixture of nitric oxide and nitrogen dioxide).

(1) 

$$2\,\mathrm{SO_2}+\mathrm{H_2O}+\mathrm{O_2}+\mathrm{N_2O_3} \rightarrow 2\,\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{O-NO}\\ \mathrm{OH}\end{matrix}\right.$$

(2) 

$$2\,\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{O-NO}\\ \mathrm{OH}\end{matrix}\right. +\mathrm{H_2O} \rightarrow 2\,\mathrm{SO_2}\left\langle\begin{matrix}\mathrm{OH}\\ \mathrm{OH}\end{matrix}\right. +\mathrm{N_2O_3}$$

In equation (1) we have the formation of the nitrosyl sulfuric acid, a white crystalline compound which is not allowed to separate. Enough steam is forced into the chambers to react with it instantly, thus forming sulfuric acid and releasing the catalyst as in equation (2). When the plant is not running properly, these crystals sometimes collect on the lead walls and on decomposing form a little nitric acid, which attacks lead.

A most convincing lecture experiment may be performed to prove the existence of nitrosyl sulfuric acid. In a very dry half-liter flask put not more than three drops of concentrated nitric acid. Pass in a very slow stream of sulfur dioxide gas from a cylinder of the liquid. At first red-brown oxides of nitrogen are seen. Note that there is some water in the nitric acid:

$$H_2O + 2\,SO_2 + N_2O_3 + O_2 \rightarrow 2\,H(NO)SO_4.$$

Now pass in just enough sulfur dioxide to make the red-brown color disappear. A frostwork of white crystals forms over the walls of the flask. These are the "chamber crystals" or nitrosyl sulfuric acid. Add water, drop by drop, to the flask. The crystals disappear with evolution of considerable heat and release of red-brown oxides of nitrogen. Now add about 50 cc. of water and test for sulfates by adding a solution of barium chloride. A white precipitate insoluble in hydrochloric acid proves that sulfuric acid was formed in the experiment.

An excess of steam is used in the chambers for two reasons. First, if the sulfuric acid forming and collecting on the floor were concentrated, it would take up the catalyst, thus stopping the whole process. Second, the lead walls would be attacked by acid of high concentration. So the "chamber acid" is only 62–70 per cent. This corresponds to a specific gravity of 1.5–1.62.

To give the gases full opportunity to react a series of from three to five chambers is provided and even then some sulfur dioxide is lost. The great volume of atmospheric nitrogen present forces the use of a chimney or stack and this is made in the form of the Gay-Lussac tower, resembling the Glover tower. Oxides of nitrogen released at the end of the last chamber would be lost to the air, ruining the process, but for the clever use of the fact that concentrated acid reacts with these oxides, forming a solution of nitrosyl sulfuric acid. The concentrated acid splashes down over the broken tile and is forced from the bottom of the Gay-Lussac to the top of the Glover tower (by compressed air), where it releases its oxides of nitrogen as previously described. Unfortunately not all the catalyst is recovered and continuous replacement from nitric acid is necessary. With the two towers only 30 to 40 pounds of sodium nitrate per ton of sulfuric acid are required. The Anaconda Copper Company reduces the number of lead chambers by getting better mixing in each chamber with a system of baffle plates or partitions.

The chamber acid is suitable for use in the manufacture of soluble phosphate fertilizer from phosphate rock, but for most purposes it must be concentrated. It is boiled down in lead pans to 77 per cent acid. A compact layer of lead sulfate forms, but protects the lead beneath. Acid above 77 per cent, however, dissolves lead sulfate (hence the presence of a little lead as impurity in commercial acid) and the work must be finished in glass, platinum, or cast iron vessels to a concentration of about 94 per cent and a specific gravity of 1.84. Although iron is readily attacked by dilute acid, it is not affected by the acid of high concentration, just the reverse of the effect on lead. To make C. P. acid the commercial grade is distilled from glass or porcelain, securing a concentration of 98 per cent. The rest is water.

Exercise 7. — Without help make a detailed drawing of the lead chamber plant, using arrows to show the flow of gases and liquids.

Exercise 8. —Why not use ten chambers since considerable loss of oxides of nitrogen occurs with five chambers?

The Contact Process. — Something was known of the contact process long before, but it was only in 1901 that the German chemist, Knietsch, made it a commercial success. A mixture of sulfur dioxide and air is led through a series of iron tubes containing a porous supporting material such as asbestos or sodium sulfate which holds the catalyst, finely divided platinum or, in some plants, iron oxide (Fe_2O_3). The most favorable temperature is 400°. Below this temperature the action is too slow, and above this temperature the equilibrium is displaced in the wrong and costly direction:

$$SO_2 + O \leftrightarrows SO_3 + 22{,}600 \text{ cal.}$$

At 400° the yield of sulfur trioxide is 98–99 per cent, at 700° only 60 per cent, and at 900° practically none. Since the reaction desired is exothermic the catalyst must be cooled somewhat by passing the cold gases around the tubes to hold the temperature to 400°. It is the universal practice to pass the sulfur trioxide into

98 per cent acid, maintaining that concentration by a sufficient stream of water. This seems absurd until we learn that the gas, or mist (SO_3) is not readily absorbed by water.

Alexander Smith (*Intermediate Chemistry*, 279) explains this very clearly. The mixture of sulfur trioxide and excess oxygen passes into water as bubbles. Naturally these bubbles are quickly saturated with water vapor and the trioxide "fumes," forming a mist of droplets of sulfuric acid. These move slowly, if at all, and so do not often touch the wall of surrounding water. The bubbles escape with small absorption. In 98 per cent acid, however, the vapor tension of water is so slight that there is but little "fuming" or droplet formation within the bubbles. Consequently the molecules of hot sulfur trioxide, dashing in all directions with a velocity greater than 1000 feet per second (faster than sound) smash into the wall of water and are caught, forming sulfuric acid, a very beautiful illustration of the relation of physics to chemistry.

The expensive platinum used as a catalyst (several times as expensive as gold) is easily "poisoned" by impurities in the sulfur dioxide, especially the oxide of arsenic, which is commonly found in the flue gases from iron pyrites and some other sulfides. Great care is taken to wash out all dust. Ferric oxide and many very cheap solids catalyze the reaction to some extent and ferric oxide is actually used in a few plants. It gives its best yield (70 per cent conversion into sulfur trioxide) at 625°.

EXERCISE 9. — Compare the two catalysts. Why can the expensive platinum compete with the cheap iron oxide?

The product of the contact process is very pure and can be made 100 per cent by adding exactly the correct amount of water. Also "fuming" acid can be made by dissolving an excess of sulfur trioxide. There is a demand for this strength.

EXERCISE 10. — Discuss the competitive features of the two great processes, lead chamber and contact.

Properties of Sulfuric Acid. — Pure anhydrous sulfuric acid is an oily colorless liquid ("oil of vitriol") with a density of 1.838 at 15°. It boils at 338° with some decomposition ($H_2SO_4 \leftrightarrows SO_3 + H_2O$). As the gases cool they combine again, forming droplets of sulfuric acid with the appearance of dense, white fumes. The constant boiling acid is 98.33 per cent. The heat of decomposition is marked at 100° and complete at 450°.

Sulfuric acid mixed with the calculated weight of water forms a hydrate ($H_2SO_4.H_2O$), a white crystalline solid melting at 8.5°. The acid mixes in all proportions with water with the evolution of much heat. To avoid sudden generation of steam and consequent spattering the concentrated acid is always slowly poured into the water (which cools it). The oxidizing power of hot, concentrated acid has already been discussed, also its dehydrating power. It removes hydrogen and oxygen in the proportion to form water from dry wood, sugar, etc., leaving black carbon. Because of its high boiling point it is nearly always used when any more volatile acid is to be released from its salts by heating the mixture:

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3.$$

On heating carefully, the other acid, practically always more volatile, is driven off continuously. Sulfuric is a moderately strong acid (see page 148). With a little water it throws off one $\overset{+}{H}$ ion. It is more difficult to throw off the second one, but at greater dilutions this is done:

$$H_2SO_4 \leftrightarrows \overset{+}{H} + \overset{-}{HSO_4}$$

$$\overset{-}{HSO_4} \leftrightarrows \overset{+}{H} + \overset{--}{SO_4}$$

Uses. — The petroleum industry was the first to demand huge quantities of sulfuric acid. Petroleum contains unsaturated compounds that darken by oxidation in air. These are removed by mixing with the concentrated acid. Much chamber acid is used direct by fertilizer factories as a means of converting calcium phosphate rock into soluble acid phosphate. The manufacture of nitroglycerin and smokeless powder calls for a large tonnage, so it is evident that this great acid was indispensable in the recent war. The tremendous importance of the Louisiana and Texas sulfur deposit now becomes apparent. Concentrated sulfuric acid is necessary to the manufacture of hydrochloric acid from salt and of nitric acid from sodium nitrate. It finds a limited demand as a rust remover from sheets of iron or steel to be tinned or galvanized.

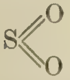
Sulfates. — Many sulfates occur in nature and many are in common use. Gypsum ($CaSO_4.2\,H_2O$), when heated with loss of three fourths of its water, becomes plaster of Paris. Mixed with water this powder "sets" to a solid. Hence its use in making plaster casts:

$$2\,CaSO_4.\,H_2O+3\,H_2O \rightarrow 2\,CaSO_4.2\,H_2O.$$

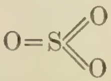
The sulfates are often called "vitriols" (from "oil of vitriol"). Green ferrous sulfate is "green vitriol," etc. All the sulfates are soluble except those of barium, strontium and lead. Calcium sulfate is soluble only to a very limited extent. The alums are double sulfates to be discussed later.

Exercise 11. — Give four methods of making calcium sulfate.

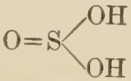
Structure of the Oxides and Acids of Sulfur. —



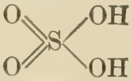
Sulfur dioxide



Sulfur trioxide



Sulfurous acid



Sulfuric acid

Other Acids of Sulfur. — When sulfur is boiled with a solution of a sulfite it adds on directly, forming a salt of *thiosulfuric acid.* The free acid is unstable:

$$Na_2SO_3+S \rightarrow Na_2S_2O_3,$$
$$Na_2S_2O_3+2\,HCl \rightarrow 2\,NaCl+H_2S_2O_3,$$
$$H_2S_2O_3 \rightarrow H_2O+SO_2+S.$$

The sodium salt is the photographer's "hypo." The name indicates that the acid differs from sulfuric acid in containing one sulfur atom in place of the fourth oxygen. "Hypo" reacts with free chlorine, and so is a good "antichlor" after bleaching.

Pyrosulfuric Acid, a good oxidizing agent, is formed when sulfuric acid and sulfur trioxide are brought together in molecular proportions. Its salts are easily prepared by heated acid sulfates:

$$2\,KHSO_4 \rightarrow H_2O+K_2S_2O_7.$$

Persulfuric Acid ($H_2S_2O_8$) is a rather modern oxidizing agent of great power. Electrolysis of a cold concentrated solution of an acid sulfate with a wire as anode produces the salts of persulfuric acid. The acid sulfate ionizes as follows:

$$KHSO_4 \leftrightarrows \overset{+}{K}+\overset{-}{HSO_4}.$$

The HSO_4 ions on discharge at the small anode unite with each other to form $H_2S_2O_8$. The acid potassium sulfate present promptly reacts with the unstable acid to form the sparingly soluble potassium persulfate, $K_2S_2O_8$. Ammonium persulfate is finding some use in photography and as a general oxidizing agent.

EXERCISE 12. — Why not electrolyze dilute solutions?

Sodium Hydrosulfite, $Na_2S_2O_4$, is made by the action of zinc and an excess sulfurous acid on sodium bisulfite:

$$Zn + 2\ NaHSO_3 + H_2SO_3 \rightarrow 2\ H_2O + ZnSO_3 + Na_2S_2O_4.$$

Its solution has great reducing power and is used to reduce blue indigo (insoluble) to indigo white (soluble) so that the dye can penetrate fabrics in the vat. Later oxidation converts the colorless product back to the blue, insoluble indigo.

EXERCISE 13. — Draw a "Sulfur Tree" somewhat like the "Oxygen Tree" on page 25.

EXERCISE 14. — How could you distinguish between a sulfide, a sulfite and a sulfate (if all were soluble)?

CHAPTER XVI

SELENIUM AND TELLURIUM. THE PERIODIC SYSTEM

Similarity of Sulfur, Selenium, and Tellurium. — These three elements resemble each other in many respects and between sulfur and selenium the likeness is remarkable. In fact, selenium usually occurs associated with sulfur in metallic sulfides. All three form similar compounds with hydrogen and oxygen and their acids and salts are much alike. Valence is the same for the three elements.

TABLE

H_2S	Hydrogen sulfide	He_2Se	Hydrogen selenide	H_2Te	Hydrogen telluride
SO_2	Sulfur dioxide	SeO_2	Selenium dioxide	TeO_2	Tellurium dioxide
H_2SO_3	Sulfurous acid	H_2SeO_3	Selenious acid	H_2TeO_3	Tellurous acid
Na_2SO_3	Sodium sulfite	Na_2SeO_3	Sodium selenite	Na_2TeO_3	Sodium tellurite
H_2SO_4	Sulfuric acid	H_2SeO_4	Selenic acid	H_2TeO_4	Telluric acid
Na_2SO_4	Sodium sulfate	Na_2SeO_4	Sodium selenate	Na_2TeO_4	Sodium tellurate

The comparison in the above table is worth noting. All three elements burn with pale blue flames to form the dioxides. Although sulfur dioxide is a gas, the other two are white solids, observed as a smoke when the elements burn. The oxides of sulfur and selenium react with water, but so far it has not been possible to hydrate the oxide of tellurium directly:

$$SO_2+H_2O \leftrightarrows H_2SO_3,$$
$$SeO_2+H_2O \leftrightarrows H_2SeO_3,$$
$$H_2TeO_3 \rightarrow TeO_2+H_2O \text{ (not reversible).}$$

Both selenious and tellurous acids are easily reduced to the element:

$$H_2SeO_3+2\,SO_2+H_2O \rightarrow Se+H_2SO_4.$$

Strong oxidizing agents convert the elements into the —ic acids:

$$S \rightarrow H_2SO_4,\ Se \rightarrow H_2SeO_4,\ Te \rightarrow H_2TeO_4.$$

Each of the three elements reacts directly with metals when heated.

Although hydrogen sulfide has an offensive odor, hydrogen selenide is worse; it smells like rotten horseradish:

$$\begin{gathered} Fe + S \rightarrow FeS, \\ Fe + Se \rightarrow FeSe, \\ Fe + Te \rightarrow FeTe. \end{gathered}$$

When these compounds are acidified poisonous gases of offensive odor are released:

$$\begin{gathered} FeS + 2\ HCl \rightarrow FeCl_2 + H_2S, \\ FeSe + 2\ HCl \rightarrow FeCl_2 + H_2Se, \\ FeTe + 2\ HCl \rightarrow FeCl_2 + H_2Te. \end{gathered}$$

When these gases are passed into water weakly acid solutions are formed and if salts be present metallic sulfides, selenides, or tellurides of various colors may be produced. It may be recalled here that a cold dish thrust into a hydrogen sulfide flame showed a spot of yellow. The unburned gas in the middle of the stream was decomposed into its elements by the heat from the outer sheath of flame. The same is true of hydrogen selenide and hydrogen telluride. The three hydrogen compounds oxidize slowly in cold air and, of course, rapidly on burning.

The striking resemblances in this group and those in the halogen family lead us to look for some general classification of the elements.

Selenium. — Both selenium and tellurium are now obtained from the anode sludge of electrolytic copper refining plants. After drying, the mud is fused with sodium nitrate to recover the precious gold and silver. Sodium selenite and sodium tellurite are formed at the same time. After extraction with water, sulfuric acid is added, which precipitates hydrated tellurium dioxide. This can later be reduced to the element by heating with carbon. The selenious acid left in solution is reduced by sulfur dioxide to the element.

Selenium is non-metallic and exists in allotropic forms. The red form is obtained by reduction of selenious acid solutions and the black form by melting the red.

Berzelius discovered this element (1817) in the flue dust of pyrite burners. Selenium colors glass a rose-red and so can neutralize the green tint of ferrous iron impurities. During the Great War the importation of Brazilian manganese into the United States was cut off through lack of ships. Selenium replaced manganese dioxide as a glass decolorizer, but only temporarily as it is too expensive for the purpose. However it is still used to a small extent in making ornamental red glass. In 1918 this country used 200,000 pounds of selenium to replace manganese and we have facilities now to produce 300,000 pounds annually if there were an extensive demand. A few hundred pounds annually suffice until the next war emergency or until some new use is discovered.

A small demand has been created by one of the curious properties of the element. Selenium conducts electricity better when exposed to light. Consequently it can be used in automatic devices for lighting buoys at night and cutting off gas flow at daylight. The selenium cell for measuring the light from stars depends on this property. By the use of selenium, pictures and drawings have been telegraphed. Wireless telephones, army signaling and other developments make use of the effect of light on conductivity of selenium. It may have a great future as a commercial element. Sulfur is used in vulcanizing rubber and perhaps selenium might be better. The so-called "sulfur-black" dyes, so cheap and serviceable, suggest selenium dyes.

Tellurium. — Tellurium is rather plentiful as gold telluride in Colorado and other mining districts, but the small quantities made so far have been extracted from the anode mud of electrolytic copper refining. There are at present facilities for making 125,000 pounds per year in this country. Tellurium has been known since 1783, but at present there is no use for it. Research is needed to make it useful. To-morrow it may become invaluable to us.

This element is really like antimony in many respects. It looks like antimony, is distinctly crystalline, resists acids and alkalies to about the same degree, and is also very brittle. Antimony is an important constituent of bearing metal alloys ("antifriction alloys"), so why not tellurium?

The selenates and tellurates of barium are insoluble like the sulfate. The following table of properties shows a steady change, with increasing atomic weight.

	SULFUR	SELENIUM	TELLURIUM
Atomic weight	32.06	79.2	127.5
Melting point	114°	170–217°	454°
Boiling point	448.5°	688°	1390°
Specific gravity	1.95–2.06	4.28–4.80	5.93–6.40

The remarkable resemblances between sulfur, selenium and tellurium, as well as in the halogen group, prepare us for a study of classification of the elements.

THE PERIODIC SYSTEM

Ever since the establishment of the atomic theory by Dalton and Berzelius, chemists have looked for some relation between the atomic weights of the elements and their properties. The development of this relation was delayed a half century because the conception of the atom became increasingly vague in spite of the brilliant work of Dalton, Berzelius, and Avogadro.

In order to come to some general understanding on atomic weights an international convention was held in 1860, and at this Cannizzaro showed the necessity of reasoning from Avogadro's hypothesis in the development of any system of atomic weights. This clarified the situation so that the epochal work of Mendeleeff and Meyer in 1869 became possible. As Wadmore says, "prior to this epoch, errors and inconsistencies must necessarily have masked any general relation between the properties and atomic weights of the elements, though vestiges of such a regularity had been observed."

It had been known that some elements were metallic or base forming and the others non-metallic or acid forming. An attempt could be made to use valence as a means of classifying elements, but this has many faults, for sodium and chlorine do not resemble each other at all, although of the same valence, and besides, several elements have more than one valence. The first ray of light on this subject appeared in 1829, when Döbereiner observed that several groups of three elements each could be so arranged that the atomic weight of one was the average of the other two and in all such cases the three elements strikingly resembled each other in properties. Chlorine (35.5), bromine (79.9), and iodine (126.9) show these relations, as the student well knows by this time. The relations are just as convincing for sulfur (32), selenium (79.2), and tellurium (127.5). Calcium (40.1), strontium (87.6), and barium (137.4) are yet to be studied, but resemble each other very closely indeed. The acceptance of Cannizzaro's ideas on atomic weights put new life into *Dobereiner's triads.* Then in 1863 Newlands, the English chemist, announced a farther-reaching relation. He arranged the elements, beginning with lithium (not hydrogen), in order of increasing atomic weight and found that "the eighth element, starting from a given one, is a kind of repetition of the first, like the eighth note of an octave in music":

Li	Be	B	C	N	O	F
6.94	9.1	11	12	14.01	16	19
K						
39.88, etc.						

Newlands read his paper before the Chemical Society of London and it was ridiculed by many chemists. Years later he was honored for his vision.

Although apparently unaware of Newlands' ideas, it was only a few years (1869) until the great Russian, Mendeleeff, outlined the periodic relations much as we know them to-day. Quite independently the German, Lothar Meyer, made a similar discovery and the credit should be divided. Mendeleeff developed the "periodic law" more fully and brilliantly than Meyer. His table, modified and brought up to date, is given below. As he stated the law, "The whole of the properties of the elements, both chemical and physical, vary in a periodic fashion with their atomic weights."

The column headed "Group O" was unknown to the authors of the system. Proceeding from lithium to the right, the chemical and physical properties steadily change. If we went no farther than fluorine, we might insist that any property of the elements changes steadily with increase in atomic weights. But such a theory would be rejected upon proceeding to the heavier element, sodium. The base-forming property steadily decreases from lithium to fluorine, but with sodium it returns in full strength. Beginning with sodium the base-forming property, for example,

THE PERIODIC TABLE

$O = 16$

	PERIODS	GROUP O R —	GROUP I R_2O —	GROUP II RO —	GROUP III R_2O_3 —	GROUP IV RO_2 RH_4	GROUP V R_2O_5 RH_3	GROUP VI RO_3 RH_2	GROUP VII R_2O_7 RH	GROUP VIII RO_4 —
Short Periods	1	He = 4	A B Li = 6.94	A B Be = 9.1	A B B = 10.9	A B C = 12	A B N = 14.01	A B O = 16	A B F = 19	
	2	Ne = 20.02	Na = 23	Mg = 24.32	Al = 27.1	Si = 28.3	P = 31.04	S = 32.06	Cl = 35.46	
Long Periods	3	A = 39.88	K = 39.10 Cu = 63.57	Ca = 40.07 Zn = 65.37	Sc = 44.1 Ga = 69.9	Ti = 48.1 Ge = 72.5	V = 51 As = 74.96	Cr = 52 Se = 79.2	Mn = 54.93 Br = 79.92	Fe = 55.84 Co = 58.97 Ni = 58.68
	4	Kr = 82.92	Rb = 85.45 Ag = 107.88	Sr = 87.63 Cd = 112.4	Y = 88.7 In = 114.8	Zr = 90.6 Sn = 118.7	Cb = 93.1 Sb = 120.2	Mo = 96 Te = 127.5	— I = 126.82	Ru = 101.7 Rh = 102.9 Pd = 106.7
	5	X = 130.2	Cs = 132.81	Ba = 137.37	La = 139	Ce = 140.25	Rare	Earth	Metals	
	6	—	Au = 197.2	Hg = 200.6	Tl = 204.0	Pb = 207.2	Ta = 181.5 Bi = 208	W = 184. —	— —	Os = 190.9 Ir = 193.1 Pt = 195.2
	7	Nt = 222	—	Ra = 226	—	Th = 232.4	—	U = 238.2	—	

again decreases until potassium is reached. But potassium hydroxide is a still stronger base than sodium hydroxide. In other words *the properties of the elements are periodic functions of their atomic weights.*

The table is so arranged that the ninth, seventeenth, etc., elements begin new horizontal rows or periods. It is seen at once that elements in the same vertical column resemble each other in valence, base-forming properties, etc. Lithium, sodium potassium, rubidium and caesium are all univalent, their hydroxides are strong, and nearly all their compounds are soluble. Moreover the free metals all react violently with water, displacing hydrogen. It can be no accident that an arrangement in periods of nine brings these elements in the same vertical column or "Group," as we call it. Nor is it an accident that sulfur, selenium and tellurium occur in the same column. Our study of the halogens prepares us to be properly impressed by the placing of chlorine, bromine, iodine and fluorine in the same group. In fact it is difficult to find any two elements of marked similarity in different columns.

Beginning with argon we must count eighteen consecutive elements, before another is found to resemble argon. This is a double period and is called a "long period" to distinguish it from those beginning with helium and neon, "short periods."

Valence Changes. — The elements of Group O are so inactive they have no combining power at all, therefore no valence. In Group I all elements are univalent and their oxides are such as Na_2O or Ag_2O (general formula, R_2O). In Group II the valence increases to two. Their oxides are such as CaO or ZnO (general formula RO). Towards oxygen the maximum valence of the different groups rises regularly to seven (R_2O_7) but toward hydrogen (or chlorine) the valence rises only to four (in Group IV) and then steadily falls to one. Chlorine in Group VII is found in Cl_2O_7 and in HCl.

Property Changes. — The elements of Group I form strong bases, those of Group II only moderately strong bases and in the middle groups, III and IV, the hydroxides are weakly basic or even weakly acidic, as in carbonic acid. Remember that most acids as well as all bases are hydroxides. Aluminum hydroxide ionizes both as a weak acid and a weak base, an "amphoteric" electrolyte, as is zinc hydroxide. In Group V the elements form strong acids such as phosphoric and nitric. Group VI permits the formation of strong acids such as sulfuric and chromic and of course Group VII is the source of the halogen acids. At the left the columns are strongly basic, at the right strongly acidic, and in the middle the elements resemble both types.

Meyer was especially interested in the regular, periodic variation in such properties as melting point, density and malleability. These change in much the same way as basicity and acidity.

There is a steady change of properties vertically as well as horizontally in the table. In any given vertical column density increases from the top to the bottom, as does the metallic character. In Group V the stability of hydrides decreases towards the bottom. Compare NH_3, PH_3, AsH_3, and SbH_3.

The Rare Gases. — Mendeleeff knew nothing of Group O. When these six elements were discovered they fitted in very well as a transition group connecting the extremely acidic elements of Group VII with the extremely basic elements of Group I. Since they are quite inactive, they have no valence and form no hydroxides.

Sub-groups. — Below sodium in Group I we observe that copper, silver and gold resemble the rest of the family mainly in valence, but resemble each other in several other ways. In Group II the zinc, cadmium and mercury make a good family, but are not remarkably like barium, calcium and strontium. In Group VII manganese has but little relation to the halogens. So each column is divided into two sub-groups, A and B, written at the two sides of the column.

Atomic Volumes. — The atomic volume of an element is its atomic weight divided by its density; it is therefore the number of cubic centimeters occupied by a gram atomic weight. If, for example, 3.18 g. of bromine occupy 1 cc. (density 3.18), it is evident that 79.92 g. (gram atomic weight) must occupy 25 cc. $\left(\frac{79.92}{3.18}\right)$. Therefore the atomic volume of bromine is 25. The atomic volumes do not increase steadily with the atomic weights but periodically. This can be shown by plotting a curve with atomic weights as abscissa and atomic volumes as ordinate (Fig. 57). The striking feature of this curve is that members of the same family occupy corresponding positions on the successive waves of the curve. Lithium, sodium, potassium, rubidium and caesium are all perched on the peaks of this mountain range. They occupy Group I in the table. Notice barium, calcium and strontium or the halogens or sulfur, selenium and tellurium.

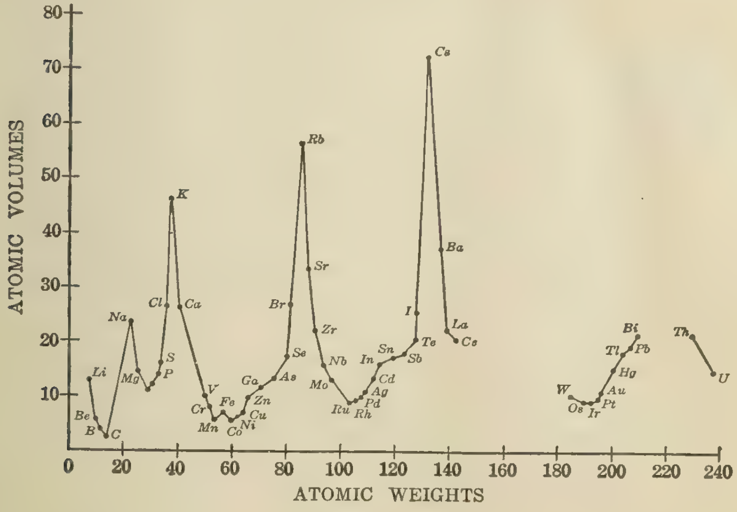


Fig. 57

Similar curves with periodic waves can be plotted for melting points and other physical properties.

Exercise 1. — Plot absolute melting points against atomic weights, using only twenty of the more common elements, to economize on time. A list of melting points follows.

Melting Points, Absolute

Li 459°	Be or Ge	1573°	Zn	692°	Fe	1800°	Ni	1725°
Na 371	Mg	924	Cd	594	Ru	2570	Pd	1820
K 335	Ca	1083	Hg	234	Os	2970	Pt	2028
Rb 311	Ba	1123						
Cs 299								

Defects of the System. — It is difficult to place hydrogen in this system, but it is usually written in Group I because of its valence and the fact that it becomes a positive ion. Possibly it is the beginning of a short period with the other members yet to be discovered.

Tellurium is next heavier than iodine, and yet if placed in this order iodine would not be grouped with chlorine, bromine and fluorine where it belongs, nor would tellurium be listed in the company of sulfur and selenium. The temptation to change places, thus putting these two elements where their properties clearly indicate they belong, is irresistible. But, written as they are in all tables, the consecutive order is broken down. Of course many attempts were made to prove that the atomic weights recorded are in error or to show that tellurium is really a compound. All of these failed. Equally annoying is the argon-potassium situation. A glance at the table shows that each conforms to the rule about "birds of a feather." But another glance at their atomic weights indicates that their places in any regular order have been interchanged.

Another weak point is the lack of quantitative relations. It is all qualitative — the properties change in a general way. And it seems unfortunate that manganese must be grouped with the halogens which it resembles so slightly. There are other examples of ill-matched elements.

Advantages. — Although we admit its imperfections we are convinced of the existence of a fundamental relation between properties and atomic weights. It has been of the greatest service in more ways than one.

1. As an aid in classifying a multitude of separate facts it helps the memory and makes for clearness.

2. By its help new elements have been predicted. A few of them were discovered later. In order to place elements where their properties indicate they belong gaps must be left here and there. The assumption is that elements exist (if we could only find them) which occupy the gaps. And from their position remarkable predictions as to their properties have been made. Mendeleeff was bold enough to predict the existence of the elements we now know as scandium, gallium and germanium. In a few years all three were discovered as a result of this prediction. It is interesting to compare prediction and actual facts in the case of gallium.

PROPERTIES OF GALLIUM

Predicted 1871	Discovered 1875
Atomic weight, about 69.	Atomic weight, 69.5.
Melting point, low.	Melting point, 30°.
Specific gravity, 5.9.	Specific gravity, 5.9.
Unacted on by air.	Only slightly oxidized.
Decompose steam at red-heat.	Decomposes steam at red-heat.
Oxide R_2O_3, Chloride RCl_3.	Oxide Ga_2O_3, Chloride $GaCl_3$.
Sulfate $R_2(SO_4)_3$.	Sulfate $Ga_2(SO_4)_3$.
Forms an alum.	Forms an alum.
Oxide more easily reducible than alumina.	Isolated by electrolysis of alkaline solution.
Metal more volatile than aluminum; discovery by spectroscope to be anticipated.	First detected by spectroscope.

Wadmore thinks the essential truth of the Periodic Law might safely rest on this testimony and that concerning scandium and germanium.

Mendeleeff made no predictions about Group O, but after the discovery of argon and helium it was evident to Sir William Ramsay, the English chemist, that there were places for three more inert gases. As the result of brilliant investigation he discovered three such gases and named them neon, krypton and xenon. Predictions were completely fulfilled in this instance. There is, however, something yet to be done in filling in the gaps. Mendeleeff predicted an element of atomic weight 100, between molybdenum and ruthenium. He placed it in Group VII and called it ekamanganese. For this we are still waiting.

EXERCISE 2. — Write a long list of properties of this missing element, the formulas of its salts, their solubility, etc.

3. *Correcting Atomic Weights.* — The failure of certain elements to fall into the group to which they evidently belong has always led to very careful redetermination of their atomic weights and in some instances errors have been discovered. This was notably true of caesium which had been given an atomic weight of 123.4. The logic of the table indicated that this was surely too low. More accurate work gave us 132.8 as the correct value quite in keeping with the Periodic Law. Mendeleeff insisted that the known atomic weights of uranium and beryllium (glucinum) must be

wrong. Later a study of vapor densities of their volatile compounds revealed the predicted errors.

Without the assistance of the Periodic Law the exact determination of the atomic weight of an element, whose compounds are all nonvolatile, becomes extremely difficult. A chemical analysis of the oxide of indium shows that this element has the equivalent (or combining) weight of 38, that is 38 g. of indium are approximately equivalent to 1 g. of hydrogen or 8 g. of oxygen. Then the correct atomic weight of indium must be some integral multiple of 38. In Mendeleeff's time $38 \times 2 = 76$ had been selected without substantial reason. But this value, 76, put indium between arsenic and selenium, where it did not belong so far as properties were concerned. Mendeleeff observed that it resembled the aluminium family and could be placed there logically if its atomic weight were $38 \times 3 = 114$. So it was ranked just after cadmium, a venture that was shortly justified by calculations based on its specific heat, as per Dulong and Petit's law. (What is this law?)

4. *Stimulating Research.* — As already shown, the gaps in the table inspire diligent effort to fill them. To this inspiration we owe the discovery of several new elements. And, as explained in detail, apparent errors in the table have led to corrections of several atomic weights. The relation of properties to atomic weights has been of the greatest value in all sorts of inorganic research and has even led to important corrections of supposed properties.

Harkins' Helix. — Many interesting modifications of the periodic table have been devised. The best of these is the one arranged by W. D. Harkins of Chicago University. He placed the elements in a helix like a spiral spring with those of a family in the same vertical column. An actual model makes the relations much clearer than a diagram. Balls representing atoms are set on a heavy wire bent in the spiral. Vertical metal rods passing through these balls line them up in the usual groups or families. The curvature of the wire is such that a rise of 1 cm. vertically (not along the wire) represents one unit of atomic weight. A vertical meter stick at the side shows this. The spiral begins with hydrogen and after it reaches titanium it pulls in toward the center, forming an inner loop (as viewed from above) containing vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc and gallium before turning out again to a full outer loop at germanium. This is the principle involved. An excellent diagram and description may be found on page 565 of McCoy and Terry's *Introduction to General Chemistry*, as well as in the *Journal of the American Chemical Society* of recent years, and in Partington's *Text Book of Inorganic Chemistry*.

Other Classifications of Elements. — It is admitted that the periodic grouping of the element in accordance with the atomic weights is not perfect. These imperfections are removed when the periodic grouping is based on *atomic numbers* instead of atomic weights.

ATOMIC NUMBERS

X-ray Spectra. — Diffraction gratings are made by ruling fine parallel lines on metal, glass, celluloid, etc. When these lines are separated by distances approximating the wave length of light a spectrum is produced by incident light similar to that formed by a common glass prism. Some gratings are marked with twenty-five thousand lines to the inch (one thousand to the millimeter).

It occurred to Laue in 1912 that if these parallel lines were closer together, separated by distances of the order of X-ray wave lengths, it should be possible to secure X-ray spectra similar to those with visible light. Now the waves in the ether known as X-rays are only one thousandth the length of light waves. To make a grating for this effect there should be ruled ten or twenty million lines to the inch, an im-

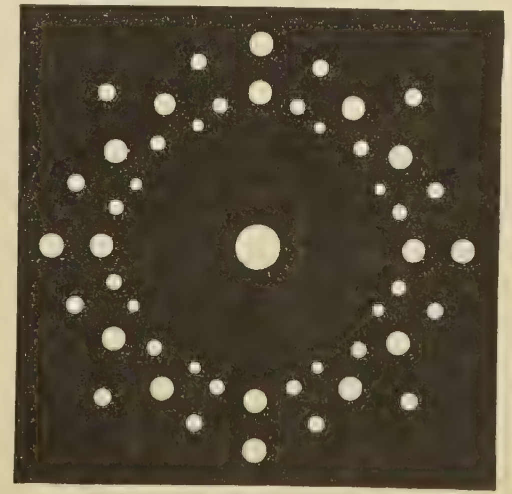


FIG. 58

possibility. Laue found such gratings already prepared in crystal surfaces. Here, as Bragg pointed out in 1914, the atoms are arranged in a geometric pattern, giving the necessary parallel lines close enough together for Laue's needs.

Figure 58 is a drawing from a photograph made by reflecting a fine beam of X-rays from a thin crystal of potassium chloride to a photograph plate. Bragg explains that each spot is due to the regular reflection of the beam of X-rays from a plane in the crystal which is especially rich in atoms. A simple cubic arrangement of atoms, as in Fig. 59, can account for the arrangement of spots in the X-ray photograph. It was found that in the diamond each carbon atom is surrounded by four others, so as to form a regular tetrahedron.

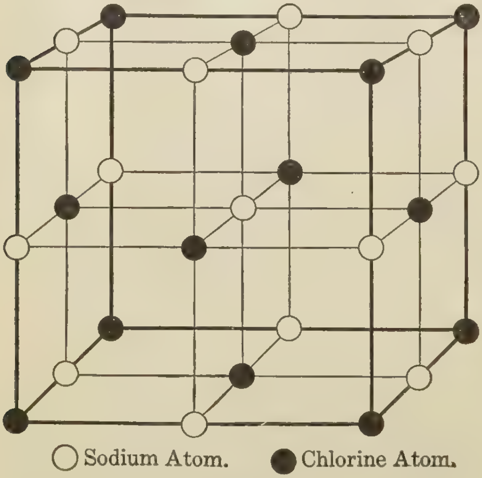


Fig. 59

Atomic Numbers. — It has been known for a quarter of a century that the cathode rays (a stream of electrons) on striking any substance in their path produce the vibrations known as X-rays. It was not until 1914 that Moseley measured the wave lengths of these rays emanating from different metals used as anti-cathodes in an evacuated X-ray tube. He made each of the metals the target (anti-cathode) of an X-ray bulb. The rays were then reflected from a large crystal of potassium ferrocyanide on to the photographic plate (Fig. 60). From the photographic spectra secured he calculated the wave lengths. These wave lengths decreased in a regular way with atomic weight. In fact Moseley found a simple numerical relation between the wave lengths of the most intense lines in the different X-ray spectra. He expressed this relation in a series of values called *atomic numbers*. Strangely enough, these are all whole numbers. The atomic numbers are approximately half the atomic weights, and represent, in reality, the number of unit positive charges of electricity in the nucleus of the atom of each element. (The student will remember that the atom is a sort of solar system made up of a positive nucleus and a number of negative electrons, all widely scattered. The weight is nearly all in the nucleus, yet this nucleus occupies only a very minute fraction of the volume of the atom.) A table of atomic numbers follows:

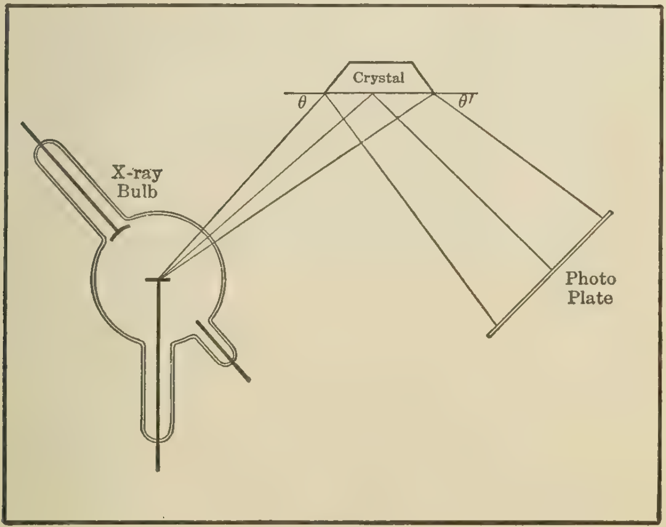


FIG. 60

ATOMIC NUMBERS (MOSELEY)

	H 1									
He 2	Li 3	Gl 4	B 5	C 6	N 7	O 8	F 9			
Ne 10	Na 11	Mg 12	Al 13	Si 14	P 15	S 16	Cl 17			
A 18	K 19	Ca 20	Sc 21	Ti 22	V 23	Cr 24	Mn 25	Fe 26	Co 27	Ni 28
	Cu 29	Zn 30	Ga 31	Ge 32	As 33	Se 34	Br 35			
K 36	Rb 37	Sr 38	Y 39	Zn 40	Cb 41	Mo 42	— 43	Ru 44	Rh 45	Pd 46
	Ag 47	Cd 48	In 49	Sn 50	Sb 51	Te 52	I 53			
Xe 54	Cs 55	Ba 56	La 57	Ce 58	Ta 73	W 74	— 75	Os 76	Ir 77	Pt 78
	Au 79	Hg 80	Tl 81	Pb 82	Bi 83	Po 84	— 85			
Nt 86	— 87	Ra 88	Ac 89	Th 90	Ux_2 91	U 92				

The atomic numbers 59–72 belong to the metals of the "rare earths," not listed in the table.

It is evident that this is superior to the periodic system of Mendeleeff, for the consecutive order is here used for argon and potassium as well as for iodine and tellurium without spoiling the group arrangement by properties. The fundamental character of an element is determined by its nuclear charge more than by its atomic weight.

It is startling to learn that Bragg measured the distances between rows of particles in crystals and found them to be of the order of the diameters of atoms. The conclusion is that there are no molecules as such in crystals but only a geometric arrangement of atoms. When dissolved or melted this physical arrangement breaks down and molecules are formed.

Exercise 3.— An element is discovered with compounds similar to those of manganese. From the analysis of its chloride the equivalent weight is found to be 49.4. What is the atomic weight? Why?

CHAPTER XVII

THE ATMOSPHERE. THE ARGON FAMILY

The earth is bathed in a great ocean of invisible gas called the atmosphere. From it animals and plants draw vast quantities of elements essential to their growth; on its motion we depend for much of our physical comfort and mental efficiency; and to its dust and moisture content we owe a great part of the natural beauty we enjoy. It carries sound, brings water from the ocean reservoir to thirsty fields and has played a great rôle in history by driving ships across the seas.

Truly the atmosphere is worthy of study. Apparently so light that it scarcely impedes our movements yet it presses upon us with a weight of nearly 15 pounds per square inch. The air resting on a single acre of earth weighs over 40,000 tons.

Air a Mixture. — About 98 per cent of air is composed of two gases, oxygen and nitrogen, and the proportions of these vary but slightly. Several other substances are present, some in proportions that vary considerably. The approximate composition of dry air is given below.

Nitrogen	78.00	per cent (Volume)
Oxygen	21.00	per cent (Volume)
Argon	0.933	per cent (Volume)
Carbon dioxide	0.03	per cent (Volume)
	99.963	

In addition to the four above named there are found water vapor, helium, neon, krypton, xenon, dust and sometimes ozone, hydrogen sulfide and oxides of nitrogen in traces. Obviously the dust content varies with the wind and other factors, and water vapor may be present in excessive amounts in the jungle, or nearly lacking over the desert.

The evidence that these various constituents are present merely as a mixture and not as one compound is convincing.

1. Each constituent of the air retains its own properties ir-

respective of the presence of the others. The oxygen is just as soluble in water as if the nitrogen were missing.

2. The properties of air are the mean of the properties of its components, which is not true of a compound. The density, for example, is what might be calculated from such a mixture.

3. When liquid air evaporates, the more volatile nitrogen tends to escape faster than the oxygen. In pure compounds, water for example, the distillate has exactly the same composition as the original liquid, unless decomposition occurred. Therefore air can be separated into its constituents by liquefaction and fractional distillation. Compounds cannot.

4. Nitrogen and oxygen can be mixed in the same proportion as found in air, without change in temperature or volume, and yet produce a mixture like air. Evidently no reaction occurs.

5. The proportions by weight cannot be represented by a chemical formula because the constituent gases are not found in exact multiples of atomic weights. This alone is a clinching argument.

Exercise 1. — Why doesn't the oxygen, heavier than nitrogen, settle and the nitrogen rise?

The Oxygen-Carbon Dioxide Balance. — It may seem alarming to learn that there are 2450 thousand million tons of carbon dioxide in the atmosphere, but this means only three parts in 10,000 of country air or twice that much in city air. We can live in air containing many times that amount of carbon dioxide.

This carbon dioxide has its source in the decay and fermentation of animal and plant bodies, in volcanic eruptions, in the respiration of animals and the combustion of fuel. The world burns over 1,300,000,000 tons of coal annually, but even so we would have to keep this up 600 years to double the present amount of carbon dioxide — if none were removed from the air. At every breath a man uses on an average 500 cc. of air and puts four per cent of carbon dioxide in it. At the same time animals are using oxygen to burn their worn-out tissues, and the combustion of fuel is consuming even more of this vital gas.

We might look into the future with fear that robbing the atmosphere of oxygen and pouring carbon dioxide into it will finally make this globe uninhabitable. But fortunately nature maintains a beautiful balance. By the catalytic action of the green chlorophyll of leaves plants utilize atmospheric carbon dioxide as food; in fact, this gas is their only source of carbon. In past ages plants were converted into coal (largely carbon) and now we burn the same coal with evolution of carbon dioxide — and heat, fortunately. Thus the cycle of carbon in nature is repeated. Providence steps in here and puts the finish of perfection on the arrangement. In utilizing carbon dioxide the plant keeps all the carbon and rejects part of the oxygen, thus purifying the air.

But this is not the only safeguard. Carbon dioxide is soluble in water, so the quantity in the ocean is vastly greater than that in the atmosphere. Shell-fish take up immense amounts for their shells (calcium carbonate).

Dust. — One of the variable components of air is dust, part of the time a nuisance and all the time a blessing. Each raindrop forms around a particle of dust as a nucleus and, for that matter, so does each minute water drop of a cloud or mist. Ionized gases also furnish nuclei, but the influence of dust is probably greater.

If a strong flask or bottle containing a little water is partially evacuated by a pump, the cooling resulting from expansion of the gas and evaporation of water produces a fog. But if the air in the bottle has first been drawn through a tube of cotton two feet long (to catch all dust) the experiment no longer results in fog formation. Dust particles or ions or something to prevent supersaturation are essential. Introduction of a little smoke (immediately after expansion) produces fog instantly.

Dust suspensions in air produce wonderful color effects. Years after the eruption of Krakatoa sunsets all over the world were especially gorgeous because such fine volcanic dust was slow to settle. Natural air has never been known to have fewer than 100 dust particles per cubic centimeter, while in cities the number ranges from 100,000 up. Yeast cells and bacteria float in the air, carrying fermentation and disease. The wind blows soil to astonishing distances. One of our richest wheat districts, the Palouse river country of Washington, received its deep, fertile soil by the aerial route from a barren district one hundred miles away.

Without dust (or gaseous ions) we should have no rain. On cooling, air would become supersaturated and a distressingly heavy dew would cover our faces, clothing, houses and the earth surface generally. We should have no soft haze to lend enchantment to distance, no twilight, no glorious sunset glows and no beautiful clouds.

Humidity. — Air can take up water vapor until the partial pressure of the water vapor equals the vapor pressure of water at that particular temperature. The humidity is then 100 per cent and the air is saturated with moisture. The student may recall that in collecting gases over water the enclosed gas had a good opportunity to become saturated. This condition is not so common in outdoor air which, although in contact with lakes, rivers and oceans, is so stirred by winds that its humidity reaches 100 per cent only when cooled sufficiently.

Air saturated at 20° has a vapor pressure of 17.5 mm. If the total pressure of the air is 750 mm., then $\frac{17.5}{750.0}$ or about 2.3 per cent of it is due to water vapor. In other words, about 2.33 per cent of the air under those conditions is water vapor. Of course each constituent gas occupies the entire volume.

Exercise 2. — What would be the weight of water in 500 cubic meters of air saturated at 23° and under a pressure of 760 mm.? Remember the use of the G. M. V.

On cooling this air to 10° the vapor pressure becomes only 9.18 mm., so the water vapor then occupies only about 1.22 per cent of the volume of the air or it would if only the water vapor were present and the pressure were kept the same. The difference between this and the amount held at 20° was precipitated as dew, fog or rain.

If, however, air saturated at 10° be warmed to 20°, it is no longer saturated, that is, if it is not in actual contact with a body of water. Its vapor pressure is still only 9.18 mm., while air at 20° is capable of holding nearly twice as much moisture. The humidity is not 100 per cent, but $\frac{9.18}{17.5}$ or 52.5 per cent.

The humidity of outdoor air averages about 66 per cent, although the seasonal variations may be great. Moist air is lighter than dry air, although it feels "heavy." The mean molecular weight of the nitrogen and oxygen in air is 28.955, but the molecular weight of water as a gas is only 18.

Sadtler states that one cubic mile of air saturated at 35° C. (95° F.) would throw down a flood of 140,000 tons of water if suddenly cooled to freezing.

Ventilation. — The old idea of correct ventilation was that the accumulation of carbon dioxide and the loss of oxygen must be prevented by introducing fresh air. The general effect was good, but not for the reasons formerly given. Carbon dioxide is not a poison and 400 parts of this gas in 10,000 parts of air (as compared with the usual 4 to 6 in 10,000) can be breathed without discomfort. Nor is a considerable reduction in the amount of oxygen such a desperate matter as was once thought. We are accustomed to an atmosphere containing about 21 per cent oxygen, yet air containing only 10 per cent will sustain life.

Some authorities believe that the oppressive feeling caused by overbreathed air is due to the decay of warm, moist, organic matter thrown off from the lungs. Others deny the existence of such poisons.

But all agree now that the humidity of the air next the skin is an important factor in ventilation. The temperature of the human body is regulated to 98.8° F. by evaporation of perspiration. Evaporation of 14 g. of water cools an average man over 0.1° C. (or half an ounce loss lowers the temperature about 0.2° F.). Nature regulates the evaporation to suit our needs. Now the layer of air in contact with the skin quickly becomes saturated and evaporation is checked unless fresh, dry air replaces this layer. Such replacement is effected by gentle air currents set up in our efforts to introduce outdoor air. Even a fan stirring the same old air produces greater comfort, although when all the stale air becomes saturated by evaporation no further relief can be secured by this device. Thus the ancient practice of bringing in fresh air is right, largely because the humidity is thus kept down, although there can be no doubt that we thrive better on an atmosphere of 21 per cent oxygen than on one not so rich. We must not go to the other extreme and reason that very dry air should be most comfortable. If too dry the air takes up moisture from the delicate mucous membranes of mouth, throat and nose at a rate that overworks them, with consequent danger from catarrh.

Modern ventilation engineers arrange for 3000 cubic feet of fresh air per hour for each person. In many great auditoriums the entire body of air is changed every ten or fifteen minutes. Opening windows is not always possible because of noise, dust or direct drafts; so ventilating fans, both blowers and exhaust fans, are resorted to. The best practice to-day calls for blowing the fresh air through a spray of water to wash out dust and introduce enough (but not too much) moisture. In removing most of the dust the bacteria are also largely removed.

The most comfortable humidity of air is from 50 per cent to 60. In winter it is almost impossible to maintain this condition in our houses. The average winter temperature of the eastern United States is about 35° F. and the outdoor humidity about 60 per cent. When this air is drawn into houses and heated to 80° F. (which is too hot) the actual weight of moisture per cubic meter remains the same, but, since warm air can carry more moisture than cold, the relative humidity falls to 22 per cent. Such air is drier, more parched, than that over the desert of Sahara. Even the houses heated to 68° F. (as they should be) do well to secure a humidity as high as 35 per cent. Under such conditions our body moisture evaporates too rapidly and we feel chilly. This results in a demand for higher temperature, with consequent extravagance at the coal bin. The desirable thing is to add water to the air so our excessive evaporation from our bodies may be restrained somewhat. The ordinary household devices are worthless. Several gallons a day must be introduced into the air of an average house to make an appreciable improvement. Unfortunately there is a limit to the introduction of moisture. If indoor humidity is much above 35 per cent, the cold window panes condense a great amount of this moisture and on very cold days are obscured with frost. The outside walls may also become damp. Of course this is true only in cold weather.

It is wise, then, to maintain the indoor temperature at 68° F. by increasing the humidity sufficiently. Such a temperature is more comfortable, and healthier, than a higher temperature accompanied by lower humidity. Efficiency, both mental and physical, is increased decidedly by securing this ideal condition. Factories, offices and schools are now benefiting greatly by attention to the humidity question. One state commission on ventilation found that by reducing the temperature of the school rooms from 78° to 68° F. the mental efficiency of the pupils was increased

35 per cent. Of course the humidity was increased as the temperature was decreased in order to keep the heat balance stable.

Liquid Air. — The liquefaction of air is an industry of considerable importance because it is the first step in securing oxygen and nitrogen for other industries. To liquefy the air it is first freed from carbon dioxide by washing with water and passing over lime. It is then subjected to high pressure, the heat of compression at 200 atmospheres being removed by cooling with running water. Under such high pressure and slightly lowered temperature the moisture in the gas is condensed. The last traces of water and carbon dioxide are absorbed by sodium hydroxide. The liquefier proper (Fig. 61) is nothing but a coil of very small copper tube with a valve to control the flow of air. The coil is contained in a

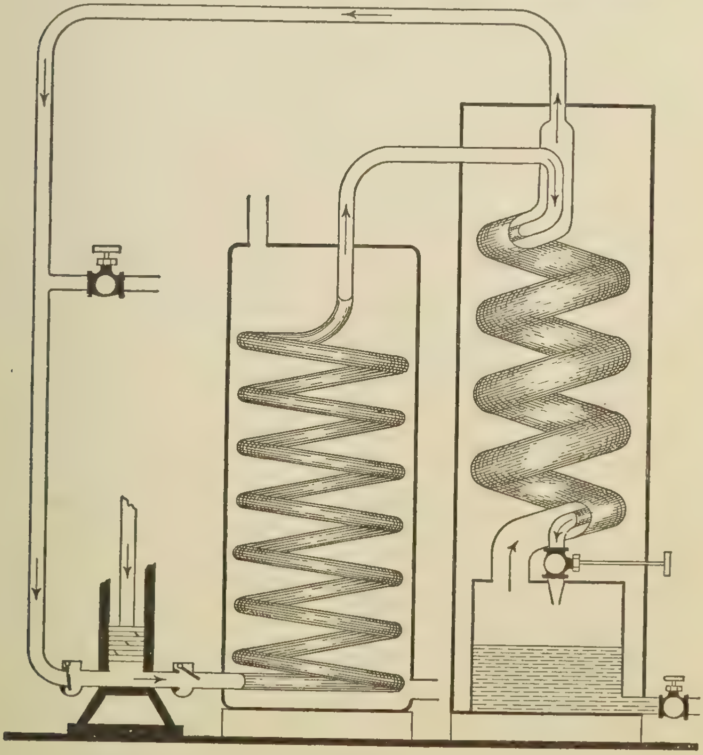


FIG. 61

metal jacket which is heat insulated with wool. On opening the valve the compressed air expands as it escapes. This cools it somewhat. It is then made to travel back through the jacket, thus further cooling the air in the copper tube. After a few minutes this progressive cooling produces a steady stream of liquid air.

To keep the air use is made of a device invented by Dewar (Fig. 62). He made a double-walled flask and evacuated the space between the two walls. A vacuum is a very poor conductor of heat. The inside walls were silvered also to reflect radiant heat. A cork stopper, loosely fitting, aided in heat insulation. Dewar found such flasks kept liquid air a surprising length of time. We use similar containers, to keep liquids hot or cold, under such names as "Thermos" bottles.

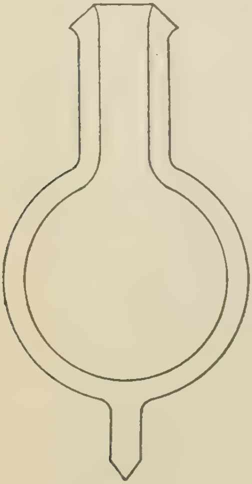


Fig. 62

Liquid air boils at −194° to −185° according to its composition. Since the nitrogen tends to evaporate first there is a steady change in composition and boiling point. Since the critical temperature is −140°, it cannot be liquefied above this temperature and at −140° about 39 atmospheres pressure are necessary to liquefy it. At lower temperatures much lower pressures suffice.

Fresh liquid air is almost colorless, but as the nitrogen escapes the bluish tint of oxygen appears. The liquid when fresh is lighter than water. Startling experiments can be performed with this liquid. In contact with it chlorine, hydrogen chloride, methane, ammonia, hydrogen sulfide and some other gases freeze to odorless liquids. Even alcohol and kerosene are persuaded to freeze by its magic touch. Metals lose much of their electrical resistance in liquid air.

The liquid oxygen left after escape of the nitrogen can be used to make high explosives (for immediate use). Charcoal wet with the proper amount of liquid oxygen explodes with the violence of dynamite if set off by a fulminating cap.

Exercise 3. — Why remove carbon dioxide and water vapor before liquefying air?

The Liquefaction of Gases. — Faraday was the father of commercial gas liquefaction. He used a combination of low temperature and high pressure. With a mixture of solid carbon dioxide and ether he secured a temperature of −80°. In 1845 Faraday had liquefied all known gases except five — hydrogen, nitrogen, oxygen, nitrous oxide and carbon monoxide — the so-called "permanent gases." In 1869 Andrews showed that for every gas there is a temperature above which it cannot be liquefied. Therefore low temperatures were the necessary factor. The truth was that Faraday failed to get those five gases cold enough. Even in later years scientists could not liquefy hydrogen at −190°. Dewar proceeded in 1898 to compress hydrogen, chill it to about −185° with liquid air, and then let the hydrogen expand. This expansion lowered the temperature below −243°, its critical temperature. Under these conditions only 11 atmospheres pressure were required to liquefy it.

About 1907 the development of the liquid air industry gave a great impetus to the manufacture of oxygen, and this in turn created a demand for compressed (not liquefied) hydrogen and acetylene for blowpipe work. In 1919 over a billion cubic feet of oxygen were made. Over $100,000,000 are invested in plants compressing various gases. It is inspiring to read the splendid chapter on this subject in the *Encyclopædia Britannica* (Liquefaction of Gases).

Exercise 4. — Read the popular account of Onnes' low-temperature work in *Harper's Magazine* (Vol. 129, 783, 1914) and report briefly.

THE ARGON FAMILY

Argon. — The fulfillment of prophecy is not confined to the Scriptures. Chemistry offers many examples. Back in 1785 Cavendish passed electric sparks through air, making the oxygen and nitrogen unite to form oxides of nitrogen, which he removed by reaction with a base. Excess oxygen was added to provide enough for all the nitrogen. Yet after removal of all the gases Cavendish could think of there was a little gas left, about 1/120 of the original volume. His partial discovery lay unused for over a century, yet it was really a sort of prediction that a new gas would some day be found in the air.

In 1895 the great English physicist, Lord Rayleigh, observed that apparently pure nitrogen made by removing everything else from air (as by Cavendish's method) was distinctly heavier than the unquestionably pure nitrogen made by decomposing ammonium nitrite. Calling in the chemist, Sir William Ramsay, to help, Rayleigh proceeded to pass the "atmospheric" nitrogen over hot magnesium, which unites with nitrogen. They found a gas left over, evidently the same residue that puzzled Cavendish, for its volume was not far from 1/120 that of the original air. Because it was chemically inert, they named the new element with the Greek word for "lazy," argon.

Ramsay used liquid air as a source of argon and found the last portions on evaporation rich in argon. This gas makes up 0.933 per cent of the air by volume. It is also found in some mineral waters, in fire damp and in some volcanic gases. Since it is so inactive it has no compounds. Millions of tungsten lamps are now filled with argon because by the use of this gas greater brilliance and longer life can be secured.

Read Rayleigh's own story of "Argon" in the *Encyclopædia Britannica.*

Helium. — The American chemist Hillebrand made a chance observation in 1889 that the uranium mineral, uraninite, on treatment with acids released a rather inactive gas (which he supposed was nitrogen). Years later Ramsay, in search of new sources of two rare gases, repeated Hillebrand's experiment, using the mineral cleveite, and secured a very inert gas different from any element then known. He found its spectrum identical with that of an element observed in the sun by Lockyer and Janssen during the solar eclipse of 1868.

They had called it helium (from the Greek, "helios," the sun). Rather astonishing to discover our new elements in the sun by lines in the solar spectrum and long afterwards to find the distant element right on our own doorstep. Soon afterward Ramsay isolated helium from the first fractions of liquid air.

Helium is so inactive that it has no compounds. It boils at 5° above absolute zero, having been liquefied by Onnes in 1908. This was the only gas left to conquer, so Onnes completed the brilliant work on liquefaction begun so well by Faraday, when he liquefied chlorine in 1823. By the rapid evaporation of liquid helium Onnes secured a temperature within 2° of absolute zero.

The romance of helium makes one of the best chapters in modern chemistry. It is closely related to the magic of radium, for every radium compound is continually releasing helium, a most astounding fact. Radium is an element in the sense that man cannot decompose it by any effort on his part. However, it is decomposing spontaneously into helium and other products. By measuring the rate of formation we are able to calculate how long it has taken the mineral fergusonite to accumulate the helium it contains. Such a calculation indicates 26,000,000 years as the age of fergusonite.

During the Great War Ramsay suggested that airships and balloons should be lifted by helium instead of hydrogen. Hydrogen, although plentiful and cheap, has its drawbacks. Flaming bullets or atmospheric electricity have ignited hydrogen balloons, but helium refuses to burn and in addition its loss by diffusion through the balloon fabric is only half as great as that of hydrogen. Although its density is twice as great as the density of hydrogen, its lifting power is 92 per cent as great. Lifting power is measured by the difference in weight of the helium (or hydrogen) and air.

Ramsay's suggestion lacked only one thing — the helium. He died at the height of the war, while still searching for a commercial source. Yet Cady, the American chemist, had previously found as much as 1.84 per cent helium in Kansas natural gas. Moore, who had worked with Ramsay, brought this neglected fact to the attention of our Chemical Warfare Service and ingenious methods were at once applied in an effort to separate helium from the natural gas. The Petrolia field of Texas, yielding about 1 per cent helium, was selected as most suitable. Just as the war closed we had commercial plants in actual operation and 150,000 cubic feet in cylinders on the New Orleans docks ready for shipment to Europe. Thus American scientists added another achievement to their long list of military scientific successes.

The United States is fortunate in owning the only workable sources of helium. Canadian gas contains some, but not enough to justify extraction. Before the war, very little helium had been secured and the cost was appalling — nearly $2000.00 per cubic foot. At this price our first shipment was worth $300,000,000.00.

However, the operators predicted an early drop to about ten cents per cubic foot. The amount needed for modern dirigibles is enormous. The R–38, now building in England for the United States, has a gas volume of 2,724,000 cubic feet.

A good war history of helium development was written by Cottrell, *Jour. Chem. Met. Eng. 20*, 104, 1919.

Krypton, Xenon, and Neon. — After the discovery of argon and helium it was apparent that there must be three or four unknown elements in the same family in order to round out the periodic table. With this incentive Ramsay carefully fractionated liquid air and obtained neon (Ne), krypton (Kr), and Xenon (X). These "rare gases," and they are truly rare, since only traces are found in the atmosphere, are quite inactive, like argon and helium. All are monatomic. Some years later, niton, a transient decomposition product of radium, was added to this group. It will be discussed later. Neon has been used in lighting tubes, but not on a commercial scale. A high vacuum tube containing pure neon glows with a beautiful and efficient light when an electric discharge passes through.

CHAPTER XVIII

NITROGEN AND AMMONIA

History of Nitrogen. — Because of its comparative inertness, nitrogen was one of the least interesting of elements until a generation ago. Now it is eagerly sought after by basic industries of war and peace. Rutherford, the Edinburgh botanist, discovered the element in 1772, but it was not really considered an element until Lavoisier studied it. He tried to name it "*azote*," but only the French accepted this name. The rest of the world called it nitrogen as soon as it was learned that it was an essential constituent of niter (KNO_3).

Occurrence. — Nitrogen is "as free as air," since it makes up four fifths of the atmosphere. The nitrogen resting on every square foot of ground weighs almost a ton, while that resting on a square mile weighs 20,000,000 tons, enough, if converted into all the combined forms desired, to meet the world's needs for 50 years.

A small amount is found in the air as ammonia and oxides of nitrogen, but this is washed into the soil by rains.

Deposits of potassium nitrate (KNO_3) or "saltpeter" are found, but are not of much consequence. Since this salt is mixed with sulfur and charcoal to make black gunpowder, it may be a matter of interest to know where manufacturers secured their nitrate a few centuries ago. Wherever nitrogenous animal refuse decayed in contact with bases, such as lime or "potash," some calcium or potassium nitrate was formed. In dry soils it appeared as a white crust on top of the ground. The soil of Mammoth Cave in Kentucky was worked for its nitrate in order to make gunpowder during the war of 1812. It was also the old custom to pile up heaps of manure with wood ashes (containing potassium carbonate) and to leach out the nitrate with water after decomposition had done its work. Deposits in India were worked for a time. Then came its manufacture from Chili saltpeter in the last century.

Sodium nitrate ($NaNO_3$), or Chili saltpeter, is one of the most important sources of nitrogen. In the rainless district of northern Chili there is a strip two miles wide by two hundred long and five feet thick that is rich in sodium nitrate. A little of the potassium salt occurs there also. By mixing solutions of sodium nitrate and potassium chloride, and manipulating the concentration and temperature, a supply of potassium nitrate more than adequate for the world's gunpowder needs is secured:

$$NaNO_3 + KCl \leftrightarrows NaCl + KNO_3.$$

This enormous deposit of sodium nitrate is also used extensively in the manufacture of nitric acid and fertilizers, so it has great economic significance. Since the discovery of the deposit in 1809, over 53,000,000 tons have been mined.

Since plants and animals eventually decay, their nitrogenous material is all-important in enriching the soil.

Remarkable deposits of guano (bird manure) rich in combined forms of nitrogen were found on certain Peruvian islands, but these are nearly exhausted.

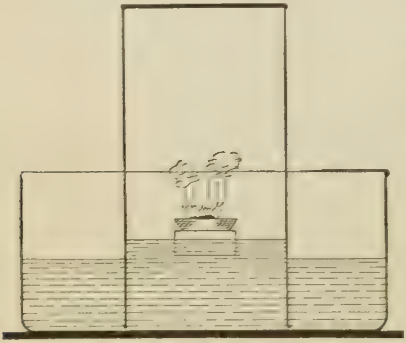


Fig. 63

Exercise 1. — If lime were mixed with a manure heap and after a time the heap leached with water, what salt would be obtained? Could you make saltpeter from it in any way?

Preparation.[1] — It is a simple matter to pass dry air over hot copper, which removes the oxygen, forming copper oxide. Commercially this oxide is then reduced back to the metal by a stream of hot hydrogen or, better, natural gas and is ready for use again. The remaining nitrogen is not quite pure, since it contains argon, carbon dioxide, etc.

If phosphorus be burned under a cylinder (Fig. 63), the oxide of phosphorus dissolves in the water, leaving the cylinder filled with nitrogen.

---

[1] Gerald Wendt of the University of Chicago has recently prepared an active form of nitrogen which is probably triatomic, N_3 (like ozone, O_3). He has also prepared a similar form of hydrogen, H_3.

Exercise 2. — Why not secure nitrogen by passing ordinary moist air over red-hot iron?

The leading commercial source of nitrogen is now liquid air. On allowing this modern product to evaporate, the more volatile nitrogen escapes first and is used in the manufacture of ammonia. It is fortunate for the cost of the process that there is a large demand for the oxygen as well.

Ammonium nitrite is an excellent laboratory source of pure nitrogen, although too expensive for commercial use. This salt is unstable, so it must be prepared when needed. Solutions of ammonium chloride and sodium nitrite are mixed and heated gently:

$$NH_4Cl + NaNO_2 \leftrightarrows NaCl + NH_4NO_2.$$

Since all four substances are soluble, this is a reversible reaction, but the equilibrium is disturned to the right on heating since gentle heating decomposes the ammonium nitrite.

Another laboratory reaction of interest occurs when ammonia is passed over hot copper oxide:

$$2\,NH_3 + 3\,CuO \rightarrow N_2 + 3\,H_2O + 3\,Cu.$$

By weighing the copper oxide, the copper and the water and collecting the nitrogen over an acid (to absorb excess ammonia), this experiment can serve as a splendid illustration of Gay-Lussac's law and as a means of determining certain equivalent weights.

Exercise 3. — If 238.71 g. of copper oxide were reduced by hot ammonia gas, how many liters of nitrogen would be obtained? How many liters of ammonia would be required?

Physical Properties. — Nitrogen is a colorless, odorless, tasteless gas, only slightly soluble in water. One liter weighs 1.2507 g., therefore it is a little lighter than air. At its critical temperature, $-146°$, it is liquefied by the critical pressure of 33 atmospheres. The liquid boils at $-195.7°$ and freezes at $-210.5°$.

Exercise 4. — What two influences prevent the heavier oxygen of the air settling to the surface of the earth, while the lighter nitrogen rises to great heights?

Chemical Properties. — Nitrogen is found free in the atmosphere because it is so inactive. However it combines with oxygen at very high temperatures and with several elements when strongly heated. With magnesium, aluminum, calcium, silicon, titanium, lithium, boron, and some other elements it forms nitrides of some interest as possible sources of ammonia:

$$3\,Mg + N_2 \rightarrow Mg_3N_2.$$

Hot calcium carbide unites with nitrogen to form calcium cyanamide. Bacteria on the roots of legumes such as clover, alfalfa, peas and beans are able to tie up the atmospheric nitrogen in a combined form available for plant growth. The union of nitrogen with hydrogen under the stimulus of a catalyst will be discussed in the ammonia section.

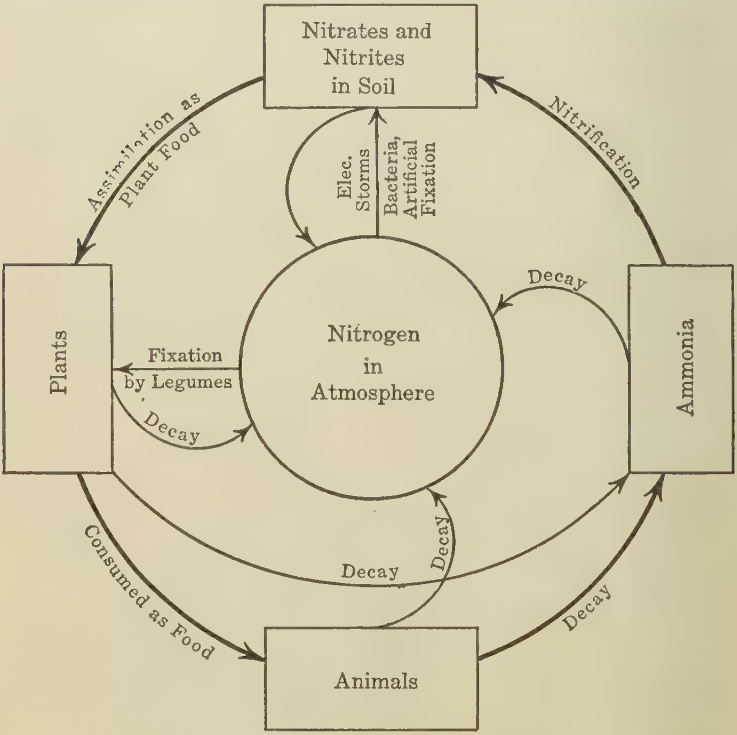


Fig. 64

Exercise 5. — The G. M. V. of nitrogen weighs 28 g. What is the formula of the gas?

The Cycle of Nitrogen in Nature. — Nitrogen is absolutely essential to plant life and hence to animal life (Fig. 64). Yet it may be feared that the available plant food in the soil will ultimately be used up. Nature has provided us to some extent with a nitrogen cycle. Atmospheric nitrogen is seized by bacteria growing on the roots of clover, alfalfa and the other legumes and converted into protein compounds. Another class of bacteria convert these proteins into nitric acid. Apparently this powerful acid would play havoc with the crops. However, there is nearly always enough basic matter in the soil to neutralize the acid, forming nitrates. In a soil deficient in bases the nitrifying bacteria refuse to work — they themselves do not enjoy an acid environment — and the farmer is forced to lime the field. When the clover is plowed under, its protein becomes a rich asset in the soil, subject to further improvement, of course, by the nitrifying bacteria. Succeeding crops of grain utilize the nitrates, animals eat the grain, and ultimately atmospheric nitrogen has become lean meat (muscle). Truly a wonderful magic! When plants or animals decay, free nitrogen is returned to the air and the cycle begins again.

Uses of Nitrogen. — We have seen that nitrogen is vital to plant and animal growth. It is now forced to react with hydrogen to form ammonia and driven to react with oxygen to form nitric oxide and thus nitric acid. When added to hot calcium carbide a good fertilizer, cyanamide, is produced. Without nitric acid and ammonia we should have practically no explosives and be greatly limited in our stock of useful dyes and drugs. An atmosphere of pure oxygen undiluted with the inert nitrogen would accelerate combustion to a dangerous degree and be too active for animal respiration.

AMMONIA

Ammonia has steadily risen in our esteem. Once of interest mainly as the pungent feature of a liniment, it later became important in the preparation of fertilizers, and during the Great War rose to the rank of a military necessity. The fate of great nations hung upon their ability to produce more and more ammonia — from which they might make nitric acid for explosives.

Priestley (1774) was the first to prepare ammonia, collecting it over mercury. However, it was left to Berthollet to determine its true composition (1785). Faraday liquefied the gas in 1823.

Traces occur in the atmosphere, but there are no earth deposits of ammonia or its derivatives. On heating animal or plant substance containing combined nitrogen ammonia is always formed. Hence the name, "spirits of hartshorn," because it was once prepared by heating deer horns, hoofs and such material. Bituminous coal contains combined nitrogen, and on distilling in absence of air great quantities of ammonia come off. Until recently this was almost the only source of this gas. It must not be imagined that there is any free ammonia locked up in the coal. Its elements merely unite during the heating.

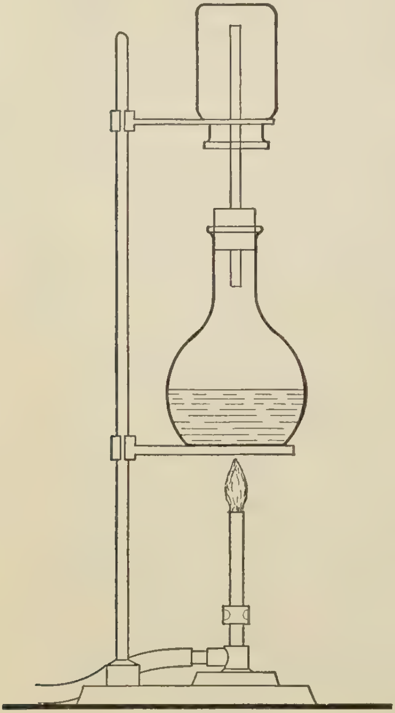


FIG. 65

EXERCISE 6. — What was the original source of the nitrogen in coal?

Preparation in the Laboratory. — The gas is conveniently prepared in the laboratory by warming a dry ammonium salt with lime or any other base. Since it is lighter than air, ammonia is collected as in Fig. 65 (why not let it displace water?):

$$NH_4Cl + NaOH \rightarrow NaCl + NH_4OH,$$
$$NH_4OH \rightarrow H_2O + NH_3.$$

The ammonium hydroxide (NH_4OH) breaks down on heating into the gas and water. In fact warming a concentrated solution of ammonium hydroxide is often found a most convenient method of securing the gas.

Nascent hydrogen reduces nitrites and nitrates to ammonia. If the hydrogen is prepared by zinc and a base, the ammonia escapes, but if prepared by zinc and an acid the ammonia neutralizes the excess acid, forming a salt.

Most protein material, when boiled with concentrated sulfuric acid, is decomposed with formation of ammonia, or rather, ammonium sulfate. This is the foundation of a famous method of food analysis.

Preparation from Coal. — Soft coal contains one per cent, or a little more, of nitrogen, and on heating in retorts without access of air enough ammonia is secured from each ton of coal to make 20 pounds of ammonium sulfate. This accounts for only a fraction of the total nitrogen, most of which remains in the coke.

Until the last few years coke was made in beehive coke ovens, allowing the ammonia and other gases to waste on the air. This was the American practice, but in Germany coal was carbonized in by-product coke ovens, which permitted the saving of all the valuable gaseous products. German efficiency in the war taught us the need of a similar saving, and in four or five years this country has made astonishing progress in installing by-product ovens, with a consequent great increase in our supplies of ammonia and its salts. When all our coke (needed in the iron industry) is produced in this way the United States will have available fully 400,000 tons of ammonium sulfate annually — and agriculture will profit proportionally. Germany secured 300,000 tons from her coke ovens in 1917.

For years Scotland has distilled her oil shales to get the oil. As a by-product enough ammonia is produced to form 42 pounds of ammonium sulfate per ton of shale.

Nitrides react with water to form ammonia:

$$Mg_3N_2 + 6\ H_2O \rightarrow 3\ Mg(OH)_2 + 2\ NH_3.$$

The Haber Process. — This process had more to do with the precipitation of the Great War by Germany, and with her near success than any other single factor.

Nitric acid is absolutely necessary to the manufacture of all explosives. Previous to 1914 it was practically all made from Chili saltpeter. But Germany, with a fleet inferior to Great Britain's, could not hope to control the seas during a war and continue importation of sodium nitrate from Chili. In short, she dared not make war until she could produce nitric acid from the air above her soil. The ammonia from her coke ovens could be oxidized into nitric acid by the Ostwald process, but it was not enough, and moreover most of it was needed to maintain soil fertility. Two methods of utilizing atmospheric nitrogen were in operation, but both required too much electrical power for a country poor in water power. The Haber process did not make excessive demands on power and suited Germany's needs perfectly. It is significant that Haber's success was assured in 1913.

Haber developed the reaction between nitrogen and hydrogen:

$$N_2+3\ H_2 \leftrightarrows 2\ NH_3.$$

At ordinary temperatures their union to form ammonia is so slow as to be imperceptible, while at high temperatures the ammonia is decomposed rapidly. In fact above 700° it is almost completely decomposed. Obviously a moderate temperature is desirable, but even so the yield is poor. Haber discovered that at 200 atmospheres pressure and 500° temperature the formation of ammonia proceeds satisfactorily if osmium or uranium be present as a catalyst. Working at such high temperatures and pressures is difficult, yet success was obtained. The Germans boasted that after the war the cheapness of the Haber process would enable them to dominate the ammonia and nitric acid markets of the world. That statement is yet to be proved at this writing.

During the war the United States spent many millions on an American improvement of Haber's process, but the engineering difficulties delayed production until too late. We have no great occasion for boasting on this score.

The necessary nitrogen was secured from liquid air and the hydrogen from water gas (see chapter on Hydrogen).

The Haber Process and Le Chatelier's Principle. — This process of making ammonia is a splendid illustration of Le Chatelier's principle. "Every force applied to a system in equilibrium causes a change which tends to relieve the effect of the force applied or to restore the previous condition." As may be seen from the equation ($N_2+3\ H_2 \leftrightarrows 2\ NH_3$) one volume of nitrogen reacts with three volumes of hydrogen to form only two volumes of ammonia. Obviously this decrease of volume tends to restore the previous pressure, so high pressure aids in the formation of ammonia.

The reaction to the right is exothermic and consequently the reaction to the left is endothermic. Heating favors a reaction that absorbs heat (endothermic), thus tending to lower the temperature. Hence to favor the formation of ammonia the temperature must be kept down. Of course all reactions are aided by heating, but in an equilibrium one may be aided more than the other. This may make a moderate temperature advisable.

EXERCISE 7. — How is this temperature influence shown in the contact process for making sulfuric acid?

The Cyanamide Process. — This method of converting atmospheric nitrogen into ammonia was one of the three great chemical supports of Germany's military machine. Yet it owed its existence to the successful manufacture of calcium carbide by Willson, an American. Calcium carbide is made by heating coke and sand in the electric furnace. The Germans, Caro and Frank, found that when nitrogen (not air) was passed over calcium carbide at about 1200° an interesting new product was formed — calcium cyanamide ($CaCN_2$). This product treated with dilute alkali steam under pressure produces ammonia. Their process was announced as a success in 1906:

$$3\,C + CaO \rightarrow CaC_2 + CO,$$
$$CaC_2 + N_2 \rightarrow CaCN_2 + C,$$
$$CaCN_2 + 3\,H_2O \rightarrow CaCO_3 + 2\,NH_3.$$

Just before the Great War Germany produced annually about 50,000 tons by this method, but expanded the output to 600,000 tons in 1916. This process was also used by the Allies to stretch their nitrogen resources. The American Cyanamide Company has been in operation at Niagara Falls since 1909 and after America's entry into the war a great plant was erected at Muscle Shoals, Alabama. It is a striking fact that this process requires startling extremes of heat and cold. The nitrogen used comes from liquid air and is added to the calcium carbide at white heat.

EXERCISE 8. — What harm would air do if passed over calcium carbide at 1000°?

Other Processes. — A process used somewhat in France and suggesting some promise is that invented by Serpek. Bauxite (hydrated Al_2O_3) and coal are heated in a revolving electric furnace while nitrogen is passed through. The aluminum nitride formed reacts with steam to release ammonia. The aluminum oxide by-product is purer than the original ore and is used in the manufacture of aluminum. But for this connection with the aluminum industry the process could not exist. Its future is uncertain:

$$Al_2O_3+3\ C+N_2 \rightarrow 2\ AlN+3\ CO,$$
$$2\ AlN+3\ H_2O \rightarrow 2\ NH_3+Al_2O_3.$$

Under the pressure of national need Professor Bucher of Brown University devised an ingenious and promising method of harnessing the valuable nitrogen of the air. The presence of iron as a catalyst aids a reaction between hot soda ash (Na_2CO_3), powdered coal, and the nitrogen of air (or of producer gas). Sodium cyanide forms and when steamed yields sodium bicarbonate and ammonia. The process may be operated cheaply in small units and has the additional advantage that several useful by-products are secured.

Physical Properties. — Ammonia is a colorless, pungent gas about one half as heavy as air. One liter weighs 0.7708 g. Its critical temperature is 130° and critical pressure 115 atmospheres. At 10° it can be liquefied with only 6.5 atmospheres. Its extreme solubility in water is noteworthy. At 20° one volume of water absorbs 700 volumes of ammonia. The gas is also quite soluble in alcohol and in ether. Its heat of evaporation is higher than that of any other known liquid except water. The concentrated solution in water has a density of 0.9 and contains about 28 per cent of the gas.

The very great solubility of ammonia in water may be shown by the experiment represented in Fig. 66. The flask is filled with dry ammonia and a few drops of water are then forced into the flask by a medicine dropper. The ammonia dissolves in these few drops, thus greatly decreasing the pressure of gas in the flask. Consequently water from the bottle is forced up the tube like a fountain. Could you do this with hydrogen chloride?

E. C. Franklin of Stanford University has done wonderful work with liquid ammonia. Compounds ionize in liquid ammonia as they do in water. Franklin's research is found in the *American Chemical Journal*, Vol. 20, pages 820 and 826; Vol. 21, page 8; Vol. 23, page 277; and Vol. 28, page 83. Also in the *Journal of the American Chemical Society*, Vol. 26, page 499 and Vol. 27, pages 192 and 820. Further reference to his work will be found under "Mercury."

Chemical Properties. — Ammonia is poisonous, air containing 1/20 of one per cent producing serious results. The gas will not burn in air but burns in oxygen. In the presence of catalysts such as platinum it reacts with oxygen to form oxides of nitrogen and water, hence nitric acid.

Ammonia will even steal oxygen from metallic oxides. Its ability to reduce hot copper oxide has been mentioned:

$$3\,CuO + 2\,NH_3 \rightarrow 3\,Cu + 3\,H_2O + N_2.$$

With sodium and potassium, ammonia reacts, when heated, to form amides. Sodamide is formed in this way:

$$2\,Na + 2\,NH_3 \rightarrow 2\,NaNH_2 + H_2.$$

Acids react with the gas to form ammonium salts, but only in the presence of at least a trace of water:

$$NH_3 + HCl \rightarrow NH_4Cl.$$

One of the most important reactions of ammonia is with water to form ammonium hydroxide:

$$NH_3 + H_2O \leftrightarrows NH_4OH.$$

Ammonia reacts with some salts. With calcium chloride it forms $CaCl_2.8\,NH_3$ and hence the gas must be dried over solid sodium hydroxide or some other dry base.

Exercise 9. — Why not dry ammonia by bubbling through concentrated sulfuric acid?

Exercise 10. — When a definite volume of ammonia is subjected to prolonged electric sparking, what happens? What volume relations hold?

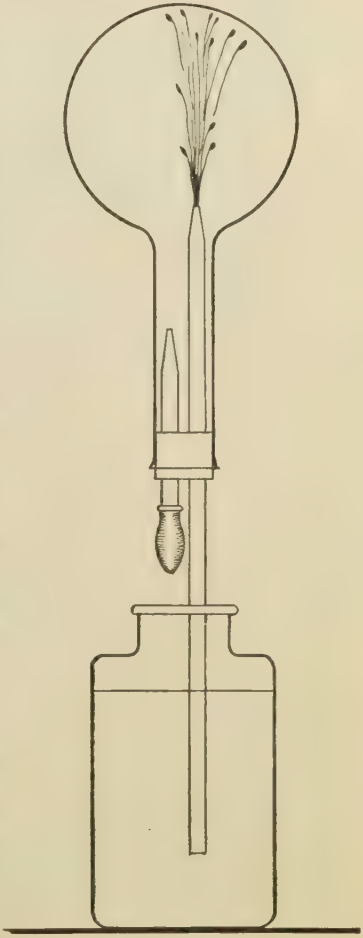


Fig. 66

Ammonium amalgam is a remarkable substance formed by adding sodium amalgam (HgNa) to a cold, concentrated solution of ammonium chloride:

$$HgNa + NH_4Cl \rightarrow NaCl + NH_4Hg.$$

The ammonium amalgam is greasy and spongy, rapidly decomposing into mercury, ammonia and hydrogen. If the amalgam be considered an alloy, it seems that we have come close to isolating the hypothetical metal ammonium.

Uses. — Ammonia is the raw material for the Ostwald process of making nitric acid. It is combined with acids to make ammonium salts used in enormous quantities for fertilizers. Its salts are used in soldering, galvanizing, in dry batteries, and the gas itself is the chief refrigerant in commercial use.

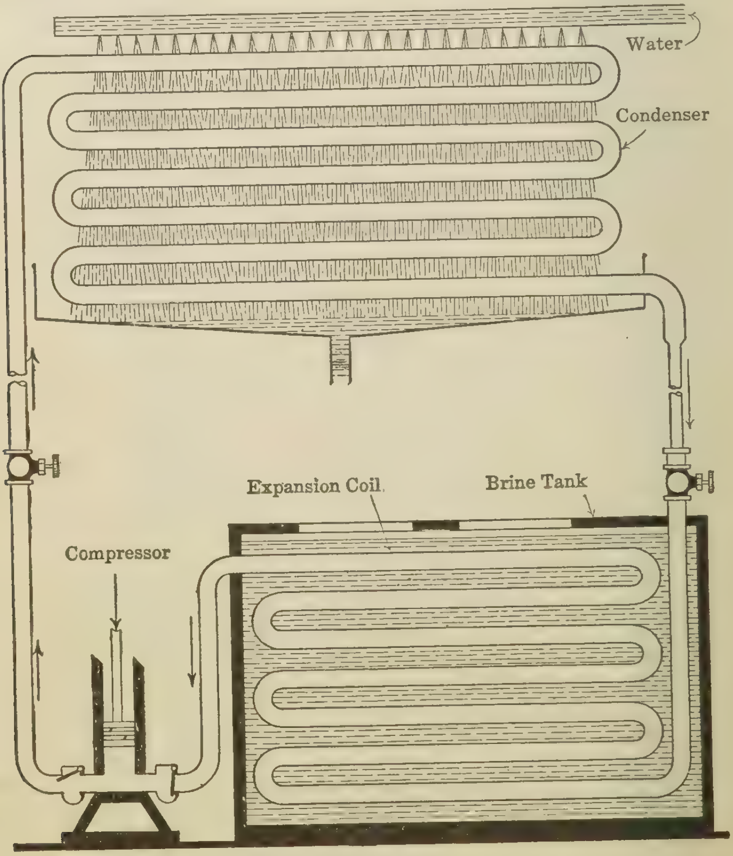


Fig. 67

In the modern ice plant ammonia under pressure is allowed to expand through a coil of metal pipe (Fig. 67). The expansion of the gas reduces the temperature of a brine surrounding the coils below the freezing point of pure water. A strong solution of calcium chloride is the usual brine, because it freezes several degrees lower than pure water. Cans of water are immersed in the brine and their contents frozen to ice. It is a simple matter to lift out the cans and empty them. In cold storage houses the rooms are chilled by pipes containing the circulating brine and no ice need be made. Household refrigerators operated by electric power are now based on this principle. Power is needed to compress the expanded ammonia ready for use again. On compression much heat is developed and this is removed by cooling the pipes with running water.

EXERCISE 11. — The heat of fusion of water is 79 calories, while the heat of evaporation of ammonia is 258 calories. How many grams of liquid ammonia must be allowed to expand to a gas in order to freeze 4 K. of ice?

Occasionally a pressure pipe bursts in a refrigerating plant and the air is filled with ammonia. Plumbers attempting to repair the breaks must wear gas masks. Sulfuric acid in the mask has been used as an absorbent, but copper sulfate is better. It unites with ammonia to form $CuSO_4.4\,NH_3$ and has none of the unpleasant features of the acid.

Ammonium Hydroxide.— Ammonia not only dissolves freely in water, but to some extent reacts with water. The equilibrium conditions are given:

$$NH_3+H_2O \leftrightarrows NH_4OH \leftrightarrows \overset{+}{N}H_4+\overset{-}{O}H.$$

Ammonium hydroxide is listed as a very weak base. Although two thirds of the ammonia present in a solution is there as dissolved molecular NH_3, according to T. S. Moore it is still true that the rest of it (NH_4OH) is only weakly ionized. The $\overset{+}{H}$ ions from any added acid removes the $\overset{-}{OH}$ ions from the field and disturbs both equilibria to the right until all dissolved ammonia has passed through the ionic stage. At −98° ammonium hydroxide is a white solid.

Ammonium Salts. — Ammonium sulfate, formed by addition of ammonia water to sulfuric acid, is the salt usually used as a fertilizer.

Ammonium chloride is useful in soldering and galvanizing. It dissociates on heating into ammonia and hydrogen chloride, which reunite on cooling with appearance of a smoke — solid particles of ammonium chloride. If heated at one end of a long tube the lighter ammonia, diffusing faster (see Graham's law), turns moist red litmus paper blue if the paper be placed at the other end.

Ammonium nitrate was used in enormous quantities during the Great War as an explosive or in explosive mixtures. It is difficult to detonate, but once started it is effective. The supply of T. N. T. was never adequate, but fortunately it was found that this expensive explosive mixed with four times its weight of the cheaper and plentiful ammonium nitrate was just as powerful.

Ammonium bicarbonate (NH_4HCO_3) is used as a partial substitute for yeast in baking crackers.

All ammonium salts decompose on heating, but they do not all release ammonia. However, any ammonium salt heated with a base releases ammonia, which can be recognized by smell or its effect on wet red litmus paper. It is the only common volatile base:

$$(1)\quad NH_4Cl + NaOH \rightarrow NaCl + NH_4OH,$$

$$(2)\quad NH_4OH \rightarrow NH_3 + H_2O.$$

Complex Ammonia Compounds. — Insoluble silver compounds dissolve in "ammonia water." Silver chloride may be used as an illustration:

$$AgCl + 2\,NH_3 \rightarrow Ag(NH_3)_2Cl.$$

On ionization the ammonia goes with the silver and in electrolysis is released at the cathode. Addition of ammonium hydroxide to a copper salt solution first precipitates copper hydroxide or, rather, a basic copper salt. Excess dissolves this, yielding a beautiful azure blue solution. With copper sulfate the product is $Cu(NH_3)_4SO_4$ and with copper chloride $Cu(NH_3)_4Cl_2$. All these complex salts yield the $\overset{++}{Cu(NH_3)_4}$ ion. The formation of the peculiar blue color, quite different from the blue of $\overset{++}{Cu}$ ion, is a test for copper compounds.

Exercise 12. — Name all the substances present in "ammonia water." There are five or six.

Other Compounds of Nitrogen and Hydrogen. — Hydrazoic acid (HN_3) is a violently explosive liquid. Its silver salt (AgN_3) is also dangerous. Hydrazine (N_2H_4) is alkaline in aqueous solution and forms salts. Hydroxylamine (NH_2OH) is apparently ammonia with the hydroxyl group in place of one hydrogen.

Soil Fertility. — About twenty years ago Sir William Crookes predicted a world wheat famine in the alarmingly near future. He believed this to be the natural result of the exhaustion of the fertility of the soil by incessant wheat cropping and the lack of adequate resources of nitrogen manures. In 70 years the Peruvian islands had yielded 11,000,000 tons of bird guano, but that deposit was nearly gone. In recent years a 10,000,000-ton deposit on a Mexican island has been opened. The sodium nitrate of Chili has served well as a fertilizer for nearly a century, but it was thought by Crookes that it could not last much longer. However, Chilian scientists now claim a long future for the industry.

The first ship load of Chili saltpeter was taken to Europe merely as ballast in 1825 and found no purchaser. It was dumped into the sea. Later its uses were developed and in 1914 the United States imported 500,000 tons of it, while Germany had been buying 750,000 tons annually.

Of about ninety elements only thirteen are necessary for crops and ten of these are found in most soils. The three that must be supplied, sooner or later, in fertilizers are nitrogen, phosphorus and potassium. Since a poor crop of wheat (13.8 bu. per acre) removes from one acre of soil 14.5 pounds of nitrogen, 10.6 pounds of phosphoric acid and 14 pounds of potash, it is evident that there is a limit to cropping without replacement. By adequate use of fertilizers the worn-out soils of Europe were made more productive than our newer soil. The average yield of wheat in Belgium is 37 bushels per acre, while in the United States it is about 15 bushels.

No wonder the gases from coke making are now captured and hundreds of thousands of tons of ammonium sulfate annually secured for the soil. But science has finally conquered the air in more ways than one. By the Birkeland-Eyde process, the cyanamide method, the Haber development, and one or two others, the world has postponed the day of a wheat famine to a very distant date. Limitless supplies of atmospheric nitrogen can now be made available for fertilizers. And of course the legumes lend material aid when given a fair chance.

Exercise 13. — What are the different catalysts that have been mentioned, and their uses?

Exercise 14. — What experiment described in this chapter proves that ammonia is composed of nitrogen and hydrogen?

Exercise 15. — How prove (three ways) that ammonia is composed of nitrogen and hydrogen?

CHAPTER XIX

NITRIC ACID AND THE OXIDES OF NITROGEN

Nitric Acid. — This acid has played a great rôle in history and is even now at the front of the stage. Its salts are essential fertilizers, without which a world wheat famine would certainly be in sight. Centuries ago one of its salts made gunpowder possible and now all of our modern high explosives which changed the map of Europe in short order are made by the use of this acid. The arts of peace, too, are finding some of its products of very great service.

The free acid was first made by the Egyptians and was employed by the alchemists. For a time the English called it "aqua fortis" while the Germans named it "saltpetersaure" to indicate that it was the acid made from saltpeter.

Preparation. — The ancient, and still the leading modern method of preparation is to heat a nitrate with concentrated sulfuric acid. In the laboratory a glass retort (Fig. 68) is used. The vapors are condensed in a cooled flask:

$$NaNO_3+H_2SO_4 \rightarrow NaHSO_4+HNO_3.$$

Cast-iron stills are used commercially and the vapors are condensed in glass tubes or, more recently, in fused quartz or duriron tubes. Duriron is an iron containing 16 per cent of silicon and is very hard and brittle. It resists corrosion by hot, concentrated nitric acid. There is some decomposition of the acid on distilling, so it is sometimes distilled under reduced pressure and consequently lower temperature:

$$4\,HNO_3 \rightarrow 4\,NO_2+O_2+2\,H_2O$$

By redistilling with concentrated sulfuric acid the water of partial decomposition is removed and by bubbling air through the distillate the red nitrogen peroxide (NO_2) is removed. The anhydrous acid is rather unstable, however, so the ordinary "concentrated" acid of commerce is made by heating sodium nitrate with somewhat diluted sulfuric acid, thus securing a product which is 68 per cent nitric acid and 32 per cent water.

The other methods of preparation which will eventually displace this simple process are described later in the chapter.

Properties. — The anhydrous nitric acid is a colorless liquid with a density of 1.52 and a boiling point of 78°. As stated before, it slowly decomposes and develops a red-brown color from dissolved oxides of nitrogen.

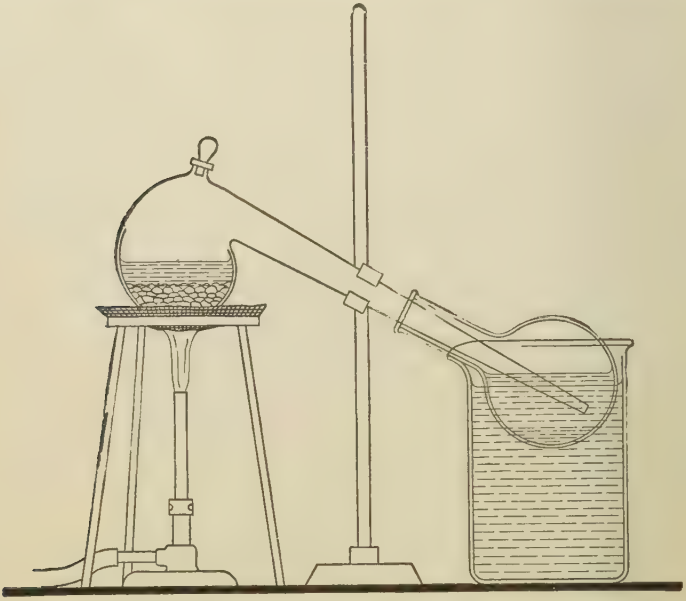


FIG. 68

When a dilute acid is distilled, water is removed first until the acid distilling over reaches 68 per cent concentration. Then there is no further change in concentration. A more concentrated acid is weakened by distillation to 68 per cent. This acid of "constant boiling point" thus makes a good standard for use and is the ordinary concentrated nitric acid of the laboratory. "Fuming" nitric acid is more active, due to the large amount of dissolved oxides of nitrogen. It is useful for special operations in organic chemistry.

Nitric acid is a "strong" acid, ionizing freely, and is somewhat unstable. As a powerful oxidizing agent it is most interesting.

1. *Action on non-metals.* Glowing carbon continues to burn in concentrated nitric acid:

$$4\,HNO_3+C \rightarrow 4\,NO_2+CO_2+2\,H_2O.$$

Sulfur heated with nitric acid is oxidized to the trioxide and in the presence of water to sulfuric acid. In fact by this treatment combined sulfur is torn out and converted into sulfuric acid. This is the basis of quantitative methods of determining the percentage of sulfur in ores and in some foods.

2. *Action on metals.* Very active metals displace hydrogen from this acid, but in most cases the hydrogen displaced is instantly oxidized by the acid and none escapes.

Less active metals such as copper are first converted into the oxide by the acid, which then dissolves the oxide. If it were not for this preliminary oxidation, nitric acid could not possibly attack metals below hydrogen in the electromotive series.

3. *Action on metallic oxides.* Oxides react readily with nitric acid, forming water and nitrates. Other reactions of interest follow:

$$CuO+2\,HNO_3 \rightarrow Cu(NO_3)_2+H_2O,$$
$$Cu(OH)_2+2\,HNO_3 \rightarrow Cu(NO_3)_2+2\,H_2O,$$
$$CuCO_3+2\,HNO_3 \rightarrow Cu(NO_3)_2+H_2O+CO_2.$$

4. *Action on organic compounds.* Cellulose (of cotton or wood) is attacked with formation of cellulose nitrates some of which are high explosives. With glycerine a similar product called nitroglycerine is produced. Toluene yields the famous T. N. T. (trinitrotoluen) and even starch is nitrated to form a powerful explosive. Yellow stains on the hand may be due to the xanthoproteic acid formed by nitric acid reacting with protein tissue.

Exercise 1. — How form barium nitrate three different ways?

Nascent State. — Since nitric acid is such a powerful oxidizing agent, it can readily be reduced. However, a stream of hydrogen gas has no effect on it. If the hydrogen be generated in the vessel containing the nitric acid, reduction occurs. Either this is because the atoms of hydrogen at the instant of release are especially active or the catalytic influence of the metal displacing the hydrogen is an important factor. Nascent hydrogen reduces nitric acid down to ammonia.

EXERCISE 2. — Add a few drops of nitric acid to a beaker filled with foam because of the action of zinc on dilute sulfuric acid. The escape of hydrogen almost ceases. Pour off the liquid, neutralize with sodium hydroxide, and smell the ammonia released. Explain with all equations.

OXIDES OF NITROGEN

N_2O	Nitrous oxide	colorless gas
NO	Nitric oxide	colorless gas
N_2O_3	Nitrogen trioxide	blue liquid at $-21°$
NO_2	Nitrogen peroxide	red-brown gas
N_2O_4	Nitrogen tetroxide	colorless gas
N_2O_5	Nitrogen pentoxide	white solid

Nitrous Oxide. — It was Priestley who in 1772 first prepared nitric oxide gas by reduction of nitric oxide with moist iron filings. Since it was thought to be poisonous, Sir Humphry Davy was a rash young man when he breathed enough of it to learn its anæsthetic properties. The hysteria occasionally produced by nitrous oxide earned for it the name "laughing gas." The gas is now made by carefully heating ammonium nitrate. (At too high temperatures ammonium nitrate may explode with terrific violence.)

$$NH_4NO_3 \rightarrow 2\,H_2O + N_2O$$

EXERCISE 3. — What other ammonium salt is heated to prepare pure nitrogen?

Liquid nitrous oxide boils at $-90°$. Since it is an endothermic compound, it is unstable, liberating 18,000 cal. per gram molecule on decomposing. Consequently such substances as charcoal, sulfur and phosphorus burn in an atmosphere of nitrous oxide almost as vigorously as in oxygen. Yet the human body is unable to utilize its oxygen content. That is why oxygen must be mixed with this gas when used as an anæsthetic. Formerly only dentists used this pleasant, quick-acting anæsthetic, but in recent years it has been widely used by surgeons.

Since nitrous oxide is rather soluble, it is usually collected over warm water.

Nitric Oxide. — Although Cavendish in 1766 made this gas by passing electric sparks through a mixture of oxygen and nitrogen, and the lightning flash in air has been doing it for ages, scientists had done almost nothing with this reaction before the present century. But suddenly it became of such great importance that war and agriculture seemed likely to depend on it.

Nitric oxide is a colorless gas slightly soluble in water. The liquid boils at −153.6°. It is not a powerful oxidizing agent, like nitrous oxide, yet rapidly burning phosphorus continues to burn in it. Sulfur is unable to take its oxygen. Since the heat of formation of nitric oxide is negative, a gram of phosphorus liberates more heat when burned in nitric oxide than when burned in oxygen. This is also true of ozone and oxygen.

This gas is easily prepared by the action of somewhat diluted nitric acid on copper:

$$3\,Cu + 8\,HNO_3 \rightarrow 3\,Cu(NO_3)_2 + 2\,NO + 4\,H_2O.$$

A very pure product is made by heating nitric acid with ferrous sulfate and sulfuric acid:

$$2\,HNO_3 + 6\,FeSO_4 + 3\,H_2SO_4 \rightarrow 3\,Fe_2(SO_4)_3 + 2\,NO + 4\,H_2O.$$

In making nitric oxide a red-brown gas is first observed and then after this product is swept out of the generating flask it is replaced by a colorless gas. The explanation is simple. Nitric oxide is colorless but reacts with oxygen of the air to form red-brown nitrogen peroxide:

$$2\,NO + O_2 \rightarrow 2\,NO_2.$$

Nitrogen Peroxide. — This very poisonous gas is made by heating pulverized lead nitrate or, in fact, the nitrate of any heavy metal:

$$Pb(NO_3)_2 \rightarrow 2\,PbO + O_2 + 2\,NO_2.$$

Concentrated nitric acid reacts with copper to release this gas:

$$4\,HNO_3 + Cu \rightarrow Cu(NO_3)_2 + 2\,H_2O + 2\,NO_2.$$

It will be noted here that dilute nitric acid on copper forms nitric oxide. The water of the dilute acid probably reacts with any nitrogen peroxide formed, producing nitric acid and nitric oxide. If it be argued that the first product, no matter what the concentration, is nitric oxide, then it can be said that concentrated nitric acid would oxidize this gas to nitrogen peroxide. Either explanation is good. In preparing nitric acid there is always some decomposition with brown nitrogen peroxide as one product.

A study of the density of this gas at different temperatures is interesting. Molecular weights calculated from the density are about 92 at 20°; 56 at 70°; and 46 at 154°. The formula NO_2 calls for a molecular weight of 46, but evidently at 20° the molecules must unite to form N_2O_4 with double this molecular weight. Then below 20° only nitrogen tetroxide (N_2O_4) exists and this dissociates completely into nitrogen peroxide (NO_2) at 154°. At intermediate temperatures a mixture of the two exists with corresponding densities. Below 20° the gas condenses to a colorless liquid, from that to 154° it is brown, and above 154° colorless. At these higher temperatures even the NO_2 dissociates:

$$\underset{\text{Colorless}}{N_2O_4} \leftrightarrows \underset{\text{Brown}}{2\ NO_2} \leftrightarrows \underset{\text{Colorless}}{2\ NO+O}$$

Nitrogen peroxide supports combustion with difficulty. Its most interesting reaction is with water:

$$\text{Cold}\ H_2O+N_2O_4 \rightarrow HNO_3+HNO_2;$$
$$\text{Hot}\ H_2O+3\ NO_2 \rightarrow 2\ HNO_3+NO.$$

The reason there is no nitrous acid (HNO_2) formed in hot water is because it is decomposed by heat.

Exercise 4. — Could NO_2 be made at 700°?

Exercise 5. — If a mixture of heated air and nitrogen peroxide were led through a tower down which a spray of water fell, what would become of the nitric oxide by-product?

Nitrogen Trioxide. — This substance is formed by cooling a mixture of nitric oxide and nitrogen peroxide to −21° and appears then as a blue liquid. It dissociates well below room temperatures, so as a gas it is really the brown mixture of $NO+NO_2$. The equilibrium changes with the temperature:

$$N_2O_3 \leftrightarrows NO_2+NO.$$

The same gas mixture is formed when arsenic trioxide (As_2O_3) is heated with concentrated nitric acid and when water is added to nitrosyl sulfuric acid. (See lead chamber process.) The catalyst in this lead chamber process is usually called nitrogen trioxide, but it is apparent now that at the temperature of the chambers only $NO+NO_2$ could exist.

Exercise 6. — What influence would an excess of air have on the equilibrium given above?

Nitrogen Pentoxide. — This white solid is prepared by removing the elements of water from pure anhydrous nitric acid with phosphorous pentoxide. It is mainly a scientific curiosity, as the anhydride of nitric acid:

$$2\,HNO_3 + P_2O_5 \rightarrow 2\,HPO_3 + N_2O_5.$$

The Birkeland-Eyde Process. — Although long known that the electric spark caused union of nitric oxide and oxygen, it was not until 1902 that two Americans, Charles B. Bradley and D. R. Lovejoy, showed that nitric acid could be made commercially by this method. They worked at Niagara Falls, using the electric arc. As often happens with pioneers, they ran out of capital.

In 1903 the Norwegians, Birkeland and Eyde, working along the same lines, achieved commercial success. By their spectacular process air is blown through an electric arc distorted to a disk six feet in diameter, by a magnetic field. This gives better contact. The nitric oxide formed unites directly with excess oxygen and this secondary product, nitrogen peroxide, is brought in contact with water to form nitric acid. The nitric oxide evolved as in equation (3) reacts with more oxygen as in (2) and is not lost.

$$(1) \qquad N_2 + O_2 \rightarrow 2\,NO$$

$$(2) \qquad 2\,NO + O_2 \rightarrow 2\,NO_2$$

$$(3) \quad \text{Hot } H_2O + 3\,NO_2 \rightarrow 2\,HNO_3 + NO$$

The temperature of the arc is 3000°–3500°. Yet the second reaction will not take place at all above 620°. Nitrogen peroxide is completely decomposed at that temperature. Therefore the hot gases are cooled as rapidly as possible to about 50° and led through a spray of water in a tower. The nitric acid formed is only of 50 per cent strength and requires concentrating. Any oxides escaping from this tower are led through a second or third splash tower. These are filled with rough lumps of limestone. The very dilute acid formed reacts with the limestone to produce calcium nitrate (Equation?), a good fertilizer. Since it is too hygroscopic for convenience in handling, it is heated to drive off half its water of crystallization, and quicklime stirred in. The dry product is sold as "nitrolime."

The equilibrium ($N_2+O_2 \leftrightarrows 2\,NO$) is reached almost instantly at 3000°, but at 800° is not reached in hundreds of years. McCoy and Terry express these facts well in the following table.

Temperature	Per cent of NO	Time of Equilibrium
1500°	0.1	12 days
2000°	1.2	30 sec.
2500°	2.6	0.1 sec.
3000°	5.3	0.0004 sec.

At 3000° about 5 per cent of the gases are converted into nitric acid oxide, while at 2000° only 1 per cent yield is obtained. Any delay in cooling past 2500°, 2000°, etc., results in a loss through the development of a new and poorer equilibrium. The great heat of the gases is utilized in raising steam under boilers for power purposes. In actual practice about 2 per cent of the gases are converted into the oxide. Cheap electric power is necessary, so Norway, which leads in that respect, can afford to adopt this process. There is a large plant operating at Notodden, Norway, and one in South Carolina.

It was once thought that this method of utilizing air nitrogen was the only hope in permanent agriculture, but the Haber and cyanamide processes have since surpassed the Birkeland-Eyde in effectiveness.

The Badische process develops a stream of sparks in an iron tube 23 feet long. The Pauling process uses an arc with a somewhat different arrangement, but in all three the electric arc is the fundamental feature.

The Ostwald Process. — The essential supplement to Haber's method of making ammonia from its elements was Ostwald's oxidation of ammonia to nitric acid:

$$\underbrace{NH_3+2\,O_2 \rightarrow}_{\text{Pt catalyst at 700°.}} HNO_3+H_2O,$$

Ammonia mixed with ten times its volume of air is passed through a gauze of platinum wire at 700°, which catalyzes the reaction. Contact of 0.01 second is sufficient. The reaction is exothermic and the right temperature is maintained by regulating the flow of the gases. As with the Birkeland-Eyde process the fundamental idea had been known for generations, but it took an

Ostwald to apply it successfully. During the Great War Germany depended on this oxidation of ammonia, and the United States spent huge sums on a plant in Alabama in an attempt to develop both the Haber and Ostwald processes for military needs. It is probable that this plant will be operated in peace times for agricultural needs.

Exercise 7. — If insufficient oxygen were mixed with the ammonia in the Ostwald process, what would be the product?

Nitrous Acid (HNO_2). — When nitrogen trioxide or a mixture of nitric oxide and nitrogen peroxide is passed into cold water, nitrous acid is formed. Hence N_2O_3 is the anhydride of nitrous acid, as N_2O_5 is the anhydride of nitric acid:

$$N_2O_3 + H_2O \leftrightarrows 2\ HNO_2.$$

The acid is quite unstable, even in solution. On release from its salts by addition of sulfuric acid, red-brown fumes are seen (unless a great excess of water be present). As stated before, nitrogen peroxide in cold water yields both nitric and nitrous acids. Nitrous acid has only limited oxidizing powers. It can oxidize hydriodic acid, but not hydrobromic. There is a growing demand for the acid in making organic dyes. Of course it is made and transported as sodium nitrite ($NaNO_2$), on account of the instability of the free acid, and mixed with sulfuric acid as used. In 1910 Germany used 5000 tons of sodium nitrite, and unofficial reports indicate that the United States now consumes 4000 tons annually. A plant near Tacoma uses the arc process in its manufacture.

Hyponitrous acid ($H_2N_2O_2$) scarcely justifies mention except in reference books. The white crystals dissolve in water, forming an unstable solution:

$$(H_2N_2O_2 \rightarrow H_2O + N_2O).$$

Nitrates and Nitrites. — Nitrates occur in nature; sodium nitrate in Chili and other countries. In Russian Turkestan there is a great deposit as yet unworked. When Siberian wheat fields need it, the deposit will be utilized. There is also a great bed of mixed sodium and calcium nitrates in Egypt, 450 miles south of Cairo and east of the Nile. This has been used in Egyptian agriculture. Potassium nitrate occurs to a limited extent in

India and is formed whenever organic matter decays in contact with wood ashes.

All nitrates are soluble except those of mercury (bivalent) and bismuth, which are hydrolyzed with formation of insoluble basic salts. However, they are soluble in the presence of nitric acid.

Nitrates are grouped in three classes according to their decomposition on heating:

$$(1)\ NH_4NO_3 \rightarrow 2\ H_2O + N_2O$$
$$(2)\ NaNO_3 \rightarrow NaNO_2 + O$$
$$(3)\ 2\ Cu(NO_3)_2 \rightarrow 2\ CuO + 4\ NO_2 + O_2$$

Ammonium nitrate is the only member of the first group. Potassium nitrate acts like sodium nitrate. Practically all other nitrates decompose like copper nitrate.

Lead is sometimes fused with sodium nitrate to aid in the removal of oxygen. The resulting nitrite is dissolved and filtered from the insoluble lead oxide formed:

$$NaNO_3 + Pb \rightarrow PbO + NaNO_2.$$

The Brown Ring Test for Nitrates. — A very delicate test for nitrates (and nitrites) makes use of the formation of the brown compound $FeSO_4.NO$. To the suspected nitrate a solution of ferrous sulfate is added and then, inclining the tube, concentrated sulfuric acid is carefully poured down the wall of the tube so two layers form. At the junction of the two layers a brown ring appears if a nitrate be present. The sulfuric acid liberates nitric acid from any nitrate, which in turn oxidizes some ferrous sulfate. The nitric oxide by-product combines with some remaining ferrous sulfate to form brown $FeSO_4.NO$.

Addition of dilute sulfuric acid to a suspected nitrate or nitrite enables one to distinguish between the two (unless a large amount of water be present). Red-brown oxides of nitrogen escape from the nitrite, but not from the nitrate.

Oxidation by Nitric Acid. — In the presence of a reducing agent dilute nitric acid breaks up, yielding three oxygen atoms for every two molecules of the acid:

$$2\ HNO_3 \rightarrow H_2O + 2\ NO + (3\ O).$$

If sulfurous acid were the reducing agent, each molecule could take up one oxygen atom, forming sulfuric acid. Therefore the two nitric acid molecules are capable of taking care of three molecules of sulfurous acid:

$$2\,HNO_3+3\,H_2SO_3 \rightarrow H_2O+2\,NO+3\,H_2SO_4.$$

Ferrous sulfate is oxidized by nitric acid as shown by the usual by-product, nitric oxide. The ferrous sulfate becomes ferric sulfate, with an increase in valence of the iron:

$$2\,\ddot{Fe}SO_4+(SO_4) \rightarrow \dddot{Fe}_2\ddot{(SO_4)}_3.$$

This extra sulfate radical (SO_4) is obtained from some free sulfuric acid present when the oxygen from nitric acid very accommodatingly unites with the hydrogen of the sulfuric acid:

$$(O)+H_2SO_4 \rightarrow H_2O+(SO_4).$$

Since we must use at least 2 HNO_3 in one equation, we have at least (3 O) for oxidizing purposes. This takes care of three molecules of sulfuric acid giving 3 (SO_4) to the ferrous sulfate. It must require 6 $FeSO_4$ to take up the 3 (SO_4).

(Trial) $HNO_3+H_2SO_4+FeSO_4 \rightarrow Fe_2(SO_4)_3+NO+H_2O$

(Balanced) $2\,HNO_3+3\,H_2SO_4+6\,FeSO_4 \rightarrow 3\,Fe_2(SO_4)_3+2\,NO+4\,H_2O$

Here we introduce a new and broader conception of oxidation. In the above reactions nitric acid caused the valence of iron to increase from two to three. The oxygen from the nitric acid did not actually add on to the ferrous sulfate, but it was used indirectly. So we may say that *oxidation is an increase in valence of the positive or central element in a compound.* It is noteworthy that the nitrogen in nitric acid has a valence of five as evident from the formula of its anhydride, N_2O_5. Yet after nitric acid has oxidized ferrous sulfate or other substances, the nitrogen appears as NO, where its valence must be two. Thus when nitric acid is itself reduced, its central element drops in valence from five to two. So we may say that *reduction is a decrease in valence of the positive or central element.*

It will be remembered that when hot concentrated sulfuric acid oxidized hydrobromic acid and other substances the sulfur usually appeared at the end as SO_2. Now the anhydride of sulfuric acid is SO_3, indicating a valence of six as compared with four in sulfur dioxide. The sulfuric acid was itself reduced with a drop in valence of sulfur

$$2\,FeCl_2+Cl_2 \rightarrow 2\,FeCl_3.$$

Here is oxidation without the use of oxygen at all. The iron increased in valence from two to three. But generate hydrogen in a solution containing some ferric chloride. It is promptly *reduced* by the nascent hydrogen:

$$FeCl_2+H \rightarrow FeCl_2+HCl.$$

Exercise 8. — When iron is dissolved by hydrochloric or sulfuric acids, is a ferrous or ferric salt formed? Why?

We spoke of nitric acid being reduced to nitric oxide. A vigorous flow of nascent hydrogen carries the reduction, the lowering of valence of nitrogen, still farther. All of the oxygen is torn away from nitrogen by the nascent hydrogen and then hydrogen begins to add on. That is why ammonia may be formed with zinc and very dilute nitric acid but not with copper.

$$\begin{array}{rl}
 & 8\,HNO_3+4\,Zn \rightarrow 4\,Zn(NO_3)_2+(8\,H)\\
 & (8\,H)+HNO_3 \rightarrow NH_3+3\,H_2O\\
 & NH_3 + HNO_3 \rightarrow NH_4NO_3\\
\hline
\text{Adding,} & 10\,HNO_3+4\,Zn \rightarrow NH_4NO_3+4\,Zn(NO_3)_2+3\,H_2O
\end{array}$$

When concentrated acid is used nitric oxide cannot be a product. It would be oxidized to nitrogen peroxide by the rest of the concentrated acid. With plenty of nitric acid on zinc (see Hydrogen Chapter) brown fumes of nitrogen peroxide are obtained.

Nitric acid oxidizes sulfur to sulfuric acid, iodine to iodic acid, powdered carbon to carbon dioxide, and red phosphorus to phosphoric acid.

Exercise 9. — Write the equations for the oxidation of sulfur by nitric acid.

Aqua Regia. — This mixture, called "royal water" because it dissolves gold, is a more powerful chloride former than hydrochloric acid or chlorine. Thus it is used in analysis to convert insoluble mercuric sulfide to soluble mercuric chloride. Three parts of concentrated hydrochloric acid are mixed with one part of concentrated nitric acid. It might be expected that the nitric acid would release chlorine from the hydrochloric acid by simple oxidation. Such is the case, but this nascent chlorine does not explain all the activity of the mixture:

$$3\ HCl+HNO_3 \rightarrow 2\ H_2O+NOCl+Cl_2.$$

The nitrosyl chloride (NOCl) formed is very active. It is a brown gas of bad odor and has been used to bleach flour.

Explosives. — Nitric acid, or its salts, is necessary in the preparation of all commercial explosives. Common black gunpowder, a mixture of sulfur, charcoal and potassium nitrate, explodes with evolution of carbon dioxide, sulfur dioxide, and nitrogen as gases and potassium sulfide as a solid. These gases occupy 300 times the volume of the powder and expand still more with the heat of reaction. Explosion is merely sudden formation and expansion of gases.

Ammonium nitrate was used in enormous quantities during the Great War as an explosive or mixed with more expensive explosives such as T. N. T. Thus it supplemented our supply of much needed T. N. T. at a critical time. Ammonium nitrate is safely handled in shells, exploding with a detonating cap:

$$2\ NH_4NO_3 \rightarrow 2\ N_2+4\ H_2O+O_2.$$

Nitroglycerine is easily produced by cold nitration of common glycerine. Concentrated sulfuric is present to take up the water formed:

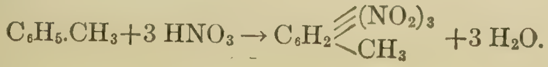
$$C_3H_5(OH)_3+3\ HNO_3 \rightarrow 3\ H_2O+C_3H_5(NO_3)_3.$$

It is a liquid exploding easily on shock, hence its transportation is dangerous. It is generally made where it is to be used. On explosion its volume is increased 12,000 times by gas formation, and the high temperature developed multiplies this about eight times:

$$4\ C_3H_5(NO_3)_3 \rightarrow 12\ CO_2+10\ H_2O+6\ N_2+O_2.$$

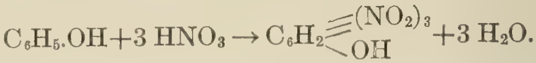
Dynamite is a mixture of nitroglycerine and wood dust or infusorial earth. Thus diluted and solidified, it is not so dangerous to handle.

Trinitrotoluene (T. N. T.) was one of the most useful of all high explosives during the recent war. Toluene, a colorless liquid secured by fractional distillation of coal tar, is nitrated as shown in the following equation:



$$C_6H_5.CH_3+3\ HNO_3 \rightarrow C_6H_2\begin{matrix}\diagup(NO_2)_3\\ \diagdown CH_3\end{matrix}+3\ H_2O.$$

Picric acid, first used in the Russo-Japanese War, is a yellow crystalline substance made by nitration of phenol ("carbolic acid"), also a derivative of coal tar:



$$C_6H_5.OH+3\ HNO_3 \rightarrow C_6H_2{<}^{(NO_2)_3}_{OH}+3\ H_2O.$$

It can be melted safely and poured into shells. Its salts are more dangerous to handle.

Guncotton is of tremendous importance, not merely as a suitable filler for torpedoes and mines but as the basis of smokeless powder. It is made by nitrating cotton. Concentrated sulfuric acid must be present to maintain the high concentration of the nitric acid (by taking up the water formed). After washing out the excess of the acids the cotton is dried. It looks like ordinary cotton:

$$2\ C_6H_{10}O_5+6\ HNO_3 \rightarrow C_{12}H_{14}(NO_3)_6+5\ H_2O.$$

When six nitrate groups are introduced a high explosive results, but with less vigorous nitration only three or four groups are introduced, forming the non-explosive pyroxylin or "soluble cotton." Guncotton burns harmlessly, but is exploded by a detonating cap. When dissolved in acetone and some vaseline added a liquid is obtained that dries to a tough horny mass, called smokeless powder. In practice the pasty mass is forced through dies so that the dried solid is perforated by small holes. On burning in the gun the surface increases and the force of explosion is not all exerted in one shattering instant but gathers strength as it progresses. In modern warfare all guns are fired with smokeless powder. Until recently wood cellulose did not nitrate properly, but under the press of necessity in the Great War a method of doing this was discovered. This made the allies independent of failure of the cotton crop as far as munitions were concerned.

Blasting gelatines like cordite are made by dissolving guncotton, nitroglycerine and vaseline in acetone. On evaporation of the acetone a horny mass results. Even starch is nitrated to yield a high explosive.

It is not to be thought that such manufacture is merely a deadly art. Without powerful explosives in great quantities there would be fewer railroad tunnels, no Panama Canal, less coal mined, less of most minerals secured, and no loosening of the hardpan where fruit trees are to be planted. Nor would so much land be cleared of stumps.

Pyroxylin, Celluloid, Artificial Silk. — The pyroxylin (lower nitrated cellulose) mentioned above dissolves in a mixture of alcohol and ether to form collodion. When this is poured on a cut the solvent evaporates and leaves a smooth transparent film of the pyroxylin. Dissolved in amyl acetate ("banana oil") it forms an excellent waterproof lacquer for protecting metals. If castor oil be added a flexible film results on drying. To prepare patent leather such a mixture containing lampblack or some colored pigment is painted repeatedly on the leather.

Celluloid is prepared by mixing pyroxylin with camphor and a little alcohol and passing through heavy rolls. This transparent material is the basis of photo films, motion picture films, celluloid toilet articles and other useful objects. Colored material may be stirred in when desired.

Artificial leather, although not so strong as the natural product, is handsome and useful. A canvas foundation is coated with a colored pyroxylin solution containing castor oil to make it flexible. After rolling it is embossed by other rolls that have the desired design engraved on their surface.

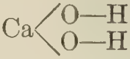
In fact the number of excellent and useful imitations of established products made possible by a clever use of pyroxylin solutions is astonishing. Among these are various expensive furs from cheaper ones, damask, eider down cloaks, brocade, carpets and artificial silk.

Artificial Silk. — Pyroxylin solution is forced through fine dies or capillary tubes and the threads, drying as they form, are denitrated in a bath of a suitable chemical. They are then spun into "silk" threads. Silk is a protein, but these denitrated fibers are restored to their original condition as cellulose, or cotton, but with an astonishing change in appearance and properties. In luster they are even more brilliant than silk, taking dyes with great beauty of effect. The artificial silk industry, although not depending on this process alone, is of some magnitude, the world's annual output reaching a value of many millions of dollars.

Structural Formulas. — Nearly all acids are made up of hydroxide groups united with a non-metal such as nitrogen or sulfur. This is not to be confused with the fact that bases are compounds of the hydroxide group with metals. The difference is that in water solution bases yield OH ions, while acids yield H ions.

The structural formula of bases is simple.

$K{-}O{-}H \qquad Na{-}O{-}H$

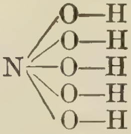


$Ca\begin{matrix} / O{-}H \\ \backslash O{-}H \end{matrix}$

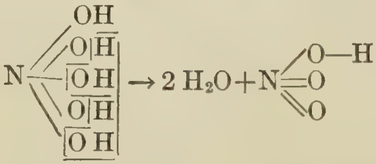
With hydroxy acids a clear conception of structure may be obtained by considering that the acid is derived from a parent acid in which the non-metal holds as many $-OH$ groups as indicated by its valence. This makes it essential to learn the correct valence of the central element. In nitric acid we learn this by noting the formula of the anhydride. The nitrogen is pentavalent:

$$2\,HNO_3 \rightarrow H_2O + N_2O_5.$$

Consequently an imaginary parent acid may be written thus:



Now this is H_5NO_5 and no such acid is known. To change from this to the ordinary HNO_3 calls for the spontaneous breaking off of $2\,H_2O$. In the diagram the second $-OH$ has lost its hydrogen.

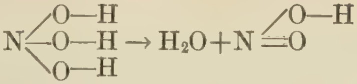


Parent acid Nitric acid

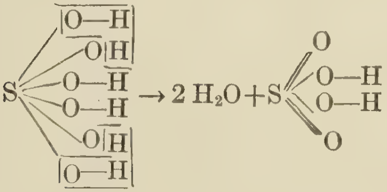
But oxygen is bivalent, so the bond of valence once used to hold the hydrogen must exert itself towards something. This suits nitrogen, for its bond of valence previously occupied in holding the third $-OH$ can extend its force to the second oxygen. The same reasoning applies to the fourth and fifth groups. This explains the two double-bonded oxygen atoms. Loss of water is neither oxidation nor reduction, so the valence of the nitrogen remains five and the valence of oxygen two.

In nitrous acid the valence of nitrogen is three ($2\,HNO_2 \rightarrow H_2O$

$+N_2O_3$). So the structure is evident. Nor is there any difficulty with sulfuric acid ($H_2SO_4 \rightarrow H_2O+SO_3$):



Parent acid Nitrous acid



Parent acid Sulfuric acid

With some acids the parent acid actually exists, as H_4SiO_4, but with most it is merely an imaginary compound. However, if it helps clarify our ideas of structure it is well worth using.

Exercise 9. — Develop the structural formula of permanganic acid, $HMnO_4$, and of dichromic acid, $H_2Cr_2O_7$.

Exercise 10. — Draw a "Nitrogen Tree" somewhat like the "Oxygen Tree" on page 25.

CHAPTER XX

THE PHOSPHORUS GROUP

Element	Atomic Weight	Density of Solid	Melting Point	Color of Solid	Hydroxides are
Nitrogen	14.08	1.0265	−210.5°	White	Strongly acidic
Phosphorus	31.04	1.83	44.10	White	Moderately acidi
Arsenic	74.96	5.73	Sublimes	Gray	Moderately acidi
Antimony	120.2	6.62	630	Silver-white	More basic than acidic
Bismuth	208.0	9.80	269	Reddish-white	Weakly basic

A glance at the Periodic Table shows that the five elements listed above resemble each other in properties. Their place in the table calls for valences of three and five and these are common except with bismuth which practically limits itself to a valence of three. But then bismuth does not conform very closely to the group resemblances, probably because its atomic weight is so much higher than the rest. With increasing atomic weights these five elements become more metallic with all that such a change involves. Nitrogen is a very strong acid-former, phosphorus less so, while the oxide of arsenic dissolves in hydrochloric acid as well as in strong bases. In other words the acidic properties of arsenic are very moderate and basic (metallic) properties are evident. This change to the basic nature is still more marked with antimony and decided with bismuth.

Furthermore the elements in the group show increasing ability to conduct heat and electricity (a characteristic property of metals) as we pass from nitrogen down the column to bismuth.

The predominant valences of three and five produce a striking similarity in the formulas of compounds. It will pay the student to compare each point brought out for one of the elements with similar facts for the other elements. As the chapter is studied the following table should be consulted again and again.

FORMULA RESEMBLANCES

ELEMENT	HYDRIDES	CHLORIDES	OXIDES	ACIDS ...	ACIDS	METALLIC COMPOUNDS
N	NH_3	NCl_3	N_2O_3, N_2O_5	$N(OH)_3 \longrightarrow HNO_2$	$N(OH)_5 \longrightarrow HNO_3$	Mg_3N_2
P	PH_3	PCl_3, PCl_5	P_2O_3, P_2O_5	$P(OH)_3$	$P(OH)_5 \longrightarrow H_3PO_4$	Ca_3P_2
As	AsH_3	$AsCl_3$, $AsCl_5$(?)	As_2O_3, As_2O_5	$As(OH)_3$	$As(OH)_5 \longrightarrow H_3AsO_4$	Zn_3As_2
Sb	SbH_3	$SbCl_3$, $SbCl_5$	Sb_2O_3, Sb_2O_5	$Sb(OH)_3$	$Sb(OH)_5 \longrightarrow H_3SbO_4$	Ca_3Sb_2
Bi		$BiCl_3$	Bi_2O_3	$Bi(OH)_3$		

This list does not include all the oxides and other compounds, but it does include the most important. A knowledge of the compounds of one element gives considerable information, by analogy, on the compounds of the others. All the hydrides are gases, like ammonia, although the others do not react with water to form bases. All the chlorides, or other halides, are hydrolyzed by water, yielding hydroxides which are more or less acidic. Most of the metallic compounds react with water to form the hydrides.

PHOSPHORUS

History. — The discovery of phosphorus was an accident. Brandt, a German alchemist, was searching for the Philosopher's Stone with which he could transform silver into gold. In 1669 he ignited dried urine with charcoal in a clay retort and secured a new substance that astonished him. It glowed in the dark when exposed to the air, hence the name given it — phosphorus (bearer of light). The preparation of the wonderful element was kept more or less secret for a century. Then Gahn and Scheele prepared it from the calcium phosphate of bone ash. Lavoisier proved it to be an element.

Occurrence. — The element is too active chemically to be found free, but as phosphorite ($Ca_3(PO_4)_2$), a fossil deposit, it is plentiful in the United States and North Africa. Apatite ($3\ Ca_3(PO_4)_2 \cdot CaF_2$), a primitive rock, occurs in large deposits in Canada. Some iron ores contain very appreciable amounts of phosphates. The hard part of bones is calcium phosphate, and organic phosphorus compounds are found in nerve tissue, muscles, and the germs of seeds. Consequently the element is essential to animal and plant growth. Egg-yolk and beans are especially rich in organic phos-

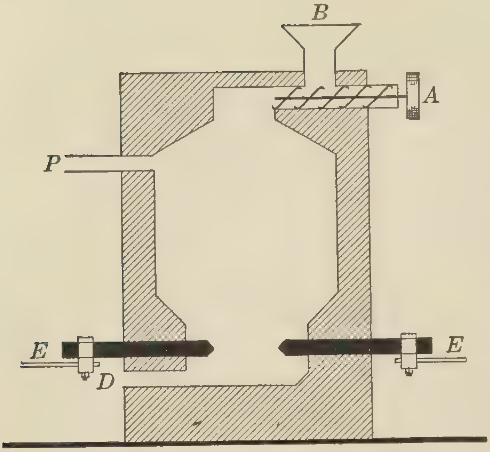


FIG. 69

phosphorus compounds, but peas and whole wheat are also valuable sources. The average human body contains 1.5 K. of combined phosphorus. Since it is a part of plant and animal tissue, it is evident that all fertile soils must contain phosphates.

Preparation. — The modern method of preparing phosphorus is to heat phosphate rock or bone ash with sand and coke in the electric furnace (Fig. 69). The charge enters the furnace from *B* by the worm feed *A*:

$$Ca_3(PO_4)_2+3\ SiO_2+5\ C \rightarrow 3\ CaSiO_3+5\ CO+2\ P.$$

The phosphorus distills off at *P* and is condensed in cold water. After filtering it is molded into small sticks and kept under water. It is entirely probable that the reaction occurs in two steps. First the silica, acting as a less volatile acid anhydride, drives off the phosphorus pentoxide, which volatilizes at that temperature:

$$Ca_3(PO_4)_2+3\ SiO_2 \rightarrow 3\ CaSiO_3+P_2O_5.$$

The carbon however reduces the oxide of phosphorus:

$$P_2O_5+5\ C \rightarrow 5\ CO+2\ P.$$

It is possible, but needlessly expensive, to make the element by heating phosphoric acid (H_3PO_4) with carbon, a fact that throws light on the reactions just given.

EXERCISE 1. — Why not heat phosphate rock, sulfuric acid and coke together to make phosphorus cheaply?

Properties. — Phosphorus exists in at least two allotropic forms, white and red, reminding us of oxygen — ozone and the different forms of sulfur.

White Phosphorus. — White phosphorus is a translucent, waxy solid, melting at 44° and boiling at 287°. Its density is 1.83 at room temperature. From the density of its vapor it is found that up to 1500° the molecule is P_4 and at 1700° it is P_2. Insoluble in water, it is readily soluble in carbon disulfide, turpentine, ether, olive oil and other liquids. From these solvents it crystallizes in the regular system. It is extremely active, combining with many elements. In warm air it ignites (about 35°), so it is always kept under water. The heat of the hand is sufficient to ignite it and serious burns may result. This form of the element is very poisonous, a fatal dose being only 0.15 g.

Exercise 2. — What was said about phosphorus in connection with ozone and also in connection with iodine?

Red Phosphorus. — When white phosphorus is heated without access of air to 230°–300° it changes to the red modification, more rapidly in the presence of a trace of iodine as a catalyst. The same change is observed on the surface of sticks of the white variety on long exposure to light. This explains the common term, "yellow phosphorus." When the red form is distilled the vapors condense to the usual white form.

The transformation from white to red involves a change in specific gravity from 1.83 to about 2.34 and as much heat is liberated, there must be less energy in the red form. This explains why the heat of combustion of the red phosphorus is less. On burning, each variety produces a dense white smoke of solid particles of the pentoxide. Red phosphorus is not soluble in any solvent, is nonpoisonous and must be heated to about 240° before it takes fire. It is microcrystalline.

When phosphorus is crystallized from molten lead a black, metallic-appearing form is obtained. Some authorities consider that the red form is merely a solution of the white in the metallic form. In support of this opinion is the fact that the color varies considerably, as does the specific gravity.

Matches. — The outstanding use of the element has always been in the manufacture of matches. Rather, since 1827, for it was then that friction matches came into general use. Until recent years the match head contained white phosphorus, an oxidizing agent such as manganese dioxide, potassium chlorate or potassium nitrate, and glue. The glue, although primarily used as an adhesive, protected the phosphorus from oxidation until the heat of friction caused it to unite almost explosively with the oxygen of the potassium chlorate. The match sticks had been dipped in melted paraffin, which after ignition of the phosphorus readily took fire and then ignited the wood. However, the workers in match factories developed horrible diseases of the bones due to constant exposure to the vapors of phosphorus. For this reason one after another of the great nations forbade the use of this element until in 1913 the United States joined this humane crusade by placing a prohibitive tax on matches made by the old method. Tetraphosphorus trisulfide (P_4S_3) was substituted. Although its odor is not exactly attractive, it is comparatively safe in manufacture and in use.

Safety matches are a special type that must be scratched on a special surface before they ignite. The head contains no phosphorus compound at all. Antimony trisulfide (Sb_2S_3) is the combustible material mixed with glue (or dextrin) and the usual oxidizing agent, which may be red lead or potassium dichromate, instead of those mentioned before. The scratching surface on the box is a mixture of powdered glass for friction, glue and red phosphorus.

Other Uses. — Most of the phosphorus produced goes into the match industry in the red form or as the sulfide. A small amount is used as a rat poison and during the Great War much was used in incendiary grenades or bombs and in making smoke screens of the pentoxide.

Chlorides. — Phosphorus reacts with chlorine, even in the cold, to form the trichloride (PCl_3), a colorless fuming liquid of density 1.6, and the pentachloride (PCl_5), a pale yellow solid. Passing more chlorine through the trichloride converts it into the pentachloride, with evolution of much heat:

$$PCl_3 + Cl_2 \rightarrow PCl_5.$$

On attempting to get the melting point of the solid it dissociates. The equilibrium is a temperature and pressure matter:

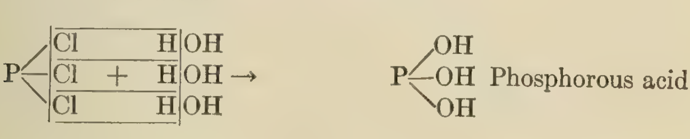
$$PCl_5 \leftrightarrows PCl_3 + Cl_2.$$

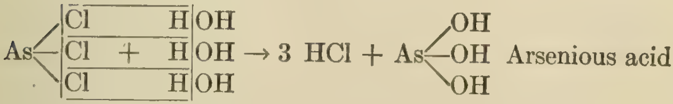
Heated in a closed tube the pressure of gases formed prevents further dissociation and the solid melts. Similar facts are true of ammonium chloride.

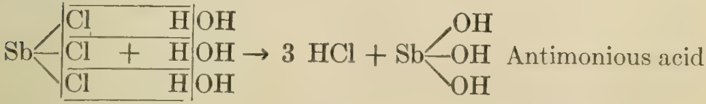
Exercise 3. — State the parallel facts for ammonium chloride.

The most interesting thing about these chlorides of phosphorus is their hydrolysis by water, a fact which shows the relations between the acids. The other halides (all formed by direct union of the elements) are the trifluoride and pentafluoride (gases), the liquid tribromide, the solid pentabromide and the solid iodides (P_2O_4 and PI_3).

The Acids of Phosphorus. — A study of the hydrolysis of the chlorides of phosphorus and the other elements of the group is of the utmost importance in giving the student a clear conception of the formula of the acids.

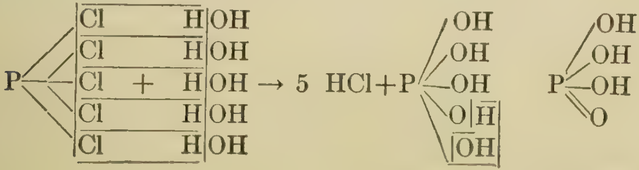






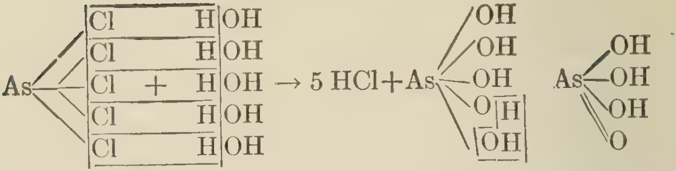
With $BiCl_3$ the hydrolysis is only partial, although the principle is the same. It will be given under Bismuth.

The reaction of water with the tribromides and triiodides is similar. Nitrogen trichloride is a dangerous explosive, so it need not be considered here.



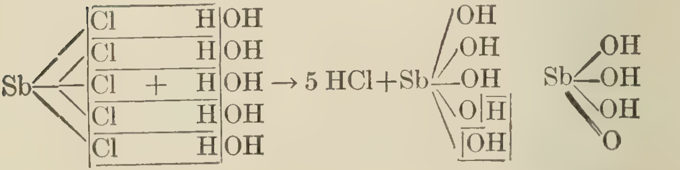
Parent phosphoric acid

Orthophosphoric acid



Parent arsenic acid

Orthoarsenic acid



Parent antimonic acid

Orthoantimonic acid

These parent acids have never been isolated so they exist for a brief instant if at all. However it is perfectly legitimate and immensely helpful to discuss their formulas as above. Their spontaneous loss of water yielding the familiar ortho acids reminds us of the explanation previously given of the structure of nitrous and nitric acids.

Orthophosphoric Acid.—All the acids of pentavalent phosphorus revert (by hydration) to orthophosphoric acid in aqueous solution. It can be made directly from the element by oxidation with nitric acid (Caution!). With white phosphorus the action may be explosive if acid of a greater specific gravity than 1.2 be used. Below that concentration the action is slow. On evaporation to a syrup which is held at 30° to 40°, colorless crystals (H_3PO_4) separate. The pure acid can also be made by reaction of water with phosphorus pentoxide. At first metaphosphoric acid (HPO_3) forms but slowly, or more rapidly if a little nitric acid be added as a catalyst; this acid adds more water, and the orthophosphoric acid (H_3PO_4) results. In other words the pentoxide is the anhydride of this acid:

$$P_2O_5 + H_2O \rightarrow 2\ HPO_3,$$
$$P_2O_5 + 3\ H_2O \rightarrow 2\ H_3PO_4.$$

The commercial acid, a thick syrupy liquid of about 85 per cent concentration, is cheaply made from phosphate rock:

$$Ca_3(PO_4)_2 + 3\ H_2SO_4 \rightarrow 3\ CaSO_4 + 2\ H_3PO_4.$$

EXERCISE 4. — If in the above reaction two thirds as much sulfuric acid were used, what would be the product? Its uses?

Pyrophosphoric Acid. — This acid, as its name indicates, is the result of heating orthophosphoric acid. At 213° water is lost as follows:

$$2\,H_3PO_4 \rightarrow H_2O + H_4P_2O_7.$$

Metaphosphoric Acid. — By heating orthophosphoric acid to 400° a greater loss of water results than in the preparation of the pyro acid, and metaphosphoric acid is formed:

$$H_3PO_4 \rightarrow H_2O + HPO_3.$$

It is also the first reaction product when the pentoxide is added to water. The pure dry acid looks like ice and is called "glacial" phosphoric acid. Like the ortho and pyro acids, it is soluble in water. It can be volatilized at a red heat.

Salts. — From the formula H_3PO_4 three types of salts are to be expected, and they are known. The sodium salts illustrate the relations:

Na_3PO_4, trisodium phosphate (the tertiary salt),
Na_2HPO_4, disodium phosphate (the secondary salt),
NaH_2PO_4, monosodium phosphate (the primary salt).

The trisodium phosphate hydrolyzes to a powerfully alkaline solution and so is often used as a washing powder. Any soluble phosphate would precipitate the salts, causing hardness of water, and in addition an alkaline solution has cleansing qualities. The salt is easily prepared by adding sodium hydroxide in large excess to the acid. Thus:

$$H_3PO_4 + 3\,NaOH \leftrightarrows Na_3PO_4 + 3\,H_2O.$$

The tendency towards reversal is here so great that it is only by the mass action of a large excess of the base that crystals of the trisodium phosphate can be secured. Heavy metals like lead form only tertiary phosphates.

If phosphoric acid be titrated with sodium hydroxide until neutral to phenolphthalein as an indicator, the disodium salt is formed. This is the sodium phosphate of the side shelf and the salt in most common use:

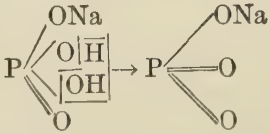
$$H_3PO_4 + 2\,NaOH \rightarrow Na_2HPO_4 + 2\,H_2O.$$

The monosodium phosphate is prepared from an equimolecular mixture of the acid and the base:

$$H_3PO_4 + NaOH \rightarrow NaH_2PO_4 + H_2O.$$

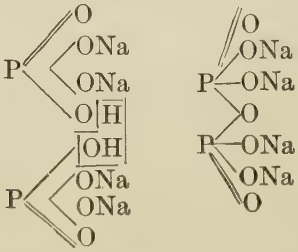
Its solution is weakly acid.

Interesting changes take place on heating the dry salts. If there are two —OH groups in one molecule they yield a molecule of water. If only one —OH is found in a molecule of the salt, then two molecules must get together in order to make the loss of water possible:



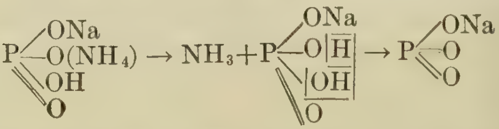
NaH_2PO_4, monosodium phosphate → $NaPO_3$, sodium metaphosphate.

Here an orthophosphate is changed into a metaphosphate. By adding an acid the free phosphoric acids could be obtained.



2 Na_2HPO_4, disodium phosphate → $Na_4P_2O_7$, sodium pyrophosphate.

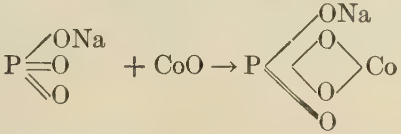
Here an orthophosphate is changed into a pyrophosphate.



$Na(NH_4)HPO_4$, microcosmic salt → NaH_2PO_4 → $NaPO_3$

Here an orthophosphate is changed to a metaphosphate.

"Microcosmic salt" is used in bead tests to detect the presence of certain salts. When heated in a loop of platinum wire the salt loses water of crystallization and then ammonia gas. This loss of NH_3 leaves an extra –OH group and further heating, now that there are two such groups, means the loss of a water molecule as diagrammed above. A metaphosphate results. The glassy bead is then touched to the substance to be tested and heated again. If a cobalt salt was tested, some oxide was probably formed by the hot flame and this oxide united directly with the sodium metaphosphate of the bead to form an orthophosphate of sodium and cobalt. This is intensely blue and is characteristic of cobalt, hence a test for it. Compare the structure of the blue compound with that of orthophosphoric acid. One hydrogen atom is replaced by a sodium atom and two hydrogen atoms by one of cobalt:



Exercise 5. — Start with the element and show how to make from it all three acids of pentavalent phosphorus.

Exercise 6. — Start with phosphorus pentoxide and make an orthophosphate. From this make a metaphosphate. From this make an orthophosphate again.

Ionization of Phosphoric Acid. — From the formula, H_3PO_4, we might conclude that each molecule could yield three hydrogen ions. The fact is that in a solution as dilute as 0.1 molar the concentration of the hydrogen is only 0.0282, so it is not a particularly strong acid. It is only the first hydrogen that ionizes at all readily:

$$H_3PO_4 \leftrightarrows \overset{+}{H} + \overset{-}{H_2PO_4}.$$

It is true that $\overset{-}{H_2PO_4}$ ionizes, yielding another hydrogen ion, but this it does to a trifling extent only:

$$\overset{-}{H_2PO_4} \leftrightarrows \overset{+}{H} + \overset{--}{HPO_4}.$$

And it is also true that $\overset{--}{HPO_4}$ yields a third hydrogen ion, but only to a very minute degree indeed:

$$\overset{--}{HPO_4} \leftrightarrows \overset{+}{H} + \overset{---}{PO_4}$$

W. H. Chapin expresses the primary, secondary and tertiary ionization very clearly as follows:

$$
\begin{array}{l}
H_3PO_4 \leftrightarrows \overset{+}{H} + H_2\overset{-}{PO_4} \text{ (Primary)} \\
\qquad\qquad\qquad\quad \overset{+}{H} \overset{\downarrow\uparrow}{+} H\overset{--}{PO_4} \text{ (Secondary)} \\
\qquad\qquad\qquad\qquad\quad \overset{+}{H} \overset{\downarrow\uparrow}{+} \overset{---}{PO_4} \text{ (Tertiary)}
\end{array}
$$

A solution of NaH_2PO_4, for example, is acid to litmus, but it is only weakly acid. A solution of Na_2HPO_4 is really slightly alkaline to litmus, due to hydrolysis, although neutral to phenolphthalein, while Na_3PO_4 hydrolyzes to form a powerfully alkaline solution. The H_2PO_4 ion is about as weak an acid as carbonic acid, but is more stable in water solution. Thus when a baking powder prepared by mixing baking soda and monosodium phosphate is moistened, carbon dioxide escapes as desired by the baker. The few H ions from the acid salt unite with the HCO_3 ions to form unstable carbonic acid:

$$NaHCO_3 + NaH_2PO_4 \rightarrow Na_2HPO_4 + H_2O + CO_2.$$

Tests for the Different Phosphates. — A neutral solution of an orthophosphate reacts with silver nitrate to form yellow silver phosphate.

White precipitates of silver pyrophosphate and silver metaphosphate leave us uncertain as to which salt we are testing. However, a solution of egg albumin is coagulated by metaphosphoric acid and the other acids have no such effect. Note that the tests with silver nitrate must be made on solutions of the salts, but the albumin test must be made with the free acids. If salt solutions are at hand, addition of acetic acid will liberate enough of the phosphoric acids. Nitric acid solutions of orthophosphates form a yellow precipitate when warmed with ammonium molybdate. The formula is too intricate for us in this year's work. With magnesia mixture a white precipitate of magnesium ammonium phosphate ($MgNH_4PO_4$) forms. These two reactions are the basis of the best methods of quantitatively determining the phosphorus in fertilizers, etc. Precipitates of exactly the same appearance and similar formula are obtained with orthoarsenates.

Other Acids. — Trivalent phosphorus forms phosphorous acid,

H_3PO_3, in large transparent crystals melting at 71°. It is dibasic in spite of its formula so although Na_2HPO_3 is possible, Na_3PO_3 is not. This acid is a strong reducing agent and when heated yields phosphine and orthophosphoric acid. (Balance the equation.)

Exercise 7. — How can phosphorous acid be made from the trichloride?

Hypophosphorous acid, H_3PO_2, is formed or, rather, its salts are formed when white phosphorus is heated with a strong solution of a base:

$$2\,P + KOH + 2\,H_2O \rightarrow PH_3 + KH_2PO_2.$$

The acid crystallizes in beautiful transparent crystals, melting at 17.4°. It is monobasic, so NaH_2PO_2 is the only type of salt possible. The salts are strong reducing agents and are of some use in medicine.

The Oxides. — The pentoxide, P_2O_5, is obtained by burning the element with free access of air. It is a white solid which reacts rather violently with water to form first metaphosphoric and finally orthophosphoric acid. So it is their anhydride. Its affinity for water is so great that it is by far the most powerful drying agent known, but not the cheapest. When moist gases pass over the white powder it becomes covered with a gummy layer of the acid and the rest of the oxide is put out of commission as a dryer. This makes it advisable to use it in thin layers only for removal of the last traces of moisture not taken out by calcium chloride or sulfuric acid. So great is the heat of formation of the pentoxide that it is a remarkably stable compound and is, in consequence, a poor oxidizing agent.

The trioxide (P_2O_3 or P_4O_6) is formed when the element is burned without enough oxygen to form the pentoxide. It is a white solid which can readily be separated from the less volatile pentoxide by heating to 173.1°, its boiling point.

Phosphine. — Phosphine (PH_3) reminds us of ammonia in formula and in its gaseous nature, but it does not react with water to form a base. However it does unite directly with hydrogen chloride, bromide and iodide to form phosphonium salts such as PH_4I, which reminds us somewhat of ammonium iodide, NH_4I. This phosphonium iodide dissociates at 30° much as does ammonium chloride at a higher temperature. It will be recalled that ammonium chloride can be melted only under pressure. In other words at higher temperatures it is stable only under increased pressure. With phosphonium chloride and bromide the same is true, except that they need the increased pressure at room temperatures.

$$PH_4I \leftrightarrows PH_3 + HI,$$
$$NH_4Cl \leftrightarrows NH_3 + HCl.$$

Phosphine is a very poisonous gas of unpleasant odor which is often spoken of as spontaneously inflammable. However, pure phosphine must be ignited before it burns. In the usual method of preparing it a liquid impurity, P_2H_4, which itself takes fire on contact with the air, ignites the phosphine. This burns, forming white clouds of the pentoxide. When the gas bubbles through water beautiful smoke rings are formed if the air in the room be quiet.

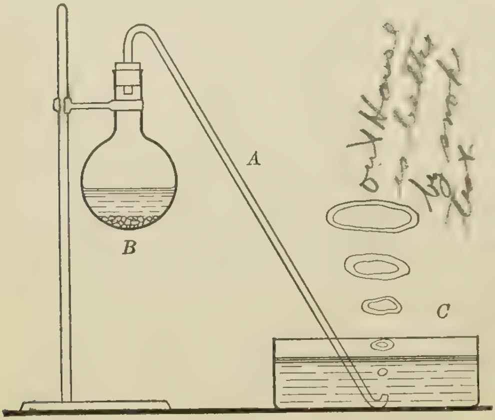


FIG. 70

bad odor? [illegible]

In the flask *B* (Fig. 70) white phosphorus is heated with a concentrated solution of potassium hydroxide. In order that no oxygen may be present in the flask a stream of ordinary illuminating gas is led through *A* for a minute or two. This sweeps out air from the flask. On heating, the phosphorus melts and the reaction begins. *C* is a wide dish of water:

$$P + KOH + H_2O \rightarrow PH_3 + KH_2PO_2.$$

Phosphine is also prepared by the action of water on phosphides. This is very similar to the formation of ammonia by the action of water on a nitride:

$$Ca_3P_2 + 6\ H_2O \rightarrow 2\ PH_3 + 3\ Ca(OH)_2,$$
$$Mg_3N_2 + 6\ H_2O \rightarrow 2\ NH_3 + 3\ Mg(OH)_2.$$

Phosphides. — Reduction of most phosphates by hot carbon yields phosphides:

$$Ca_3(PO_4)_2+8\ C \rightarrow Ca_3P_2+8\ CO.$$

The iron phosphate in some ores is reduced by hot coke in the blast furnace and the product dissolves in the molten pig iron, from which it must later be removed.

Phosphides of some metals are also made by direct union of the two elements. Calcium phosphide may be made by heating phosphorus and calcium under kerosene (to exclude air).

Sulfides. — Phosphorus and sulfur react when heated to form P_4S_3, P_4S_7 or P_2S_5, depending on the proportions taken. As soon as the reaction starts the flame is withdrawn. The tetraphosphorus trisulfide (P_4S_3) is of special interest because of its safe use in the manufacture of matches. Red phosphorus must be used in the preparation of sulfides because the yellow form reacts rather explosively.

Phosphate Fertilizers. — Since plants contain phosphorus compounds, soils must contain phosphates or must be fertilized properly. Although most fertile soils actually contain such compounds heavy cropping finally exhausts the supply and phosphates must be added. Of course plants can utilize only soluble phosphates, so the common practice is to treat ground calcium phosphate rock with enough sulfuric acid to form the soluble primary calcium phosphate (only one hydrogen of each molecule of the acid replaced by a metal), or as it is called commercially, "superphosphate":

$$Ca_3(PO_4)_2+2\ H_2SO_4 \rightarrow Ca(H_2PO_4)_2+2\ CaSO_4.$$

In recent years farmers have learned that ground phosphate rock plowed under with a green forage crop or manure is made soluble in reasonable time by the acids of decaying organic matter. This ground rock is cheaper than superphosphate.

The world uses 5,000,000 tons of phosphate rock yearly and the United States produces fully one half of this total. Here is a strategic resource in a prolonged war, and in peace an economic bargaining weapon of great importance. Civilized nations must have phosphate rock. France is in control of most of the deposits that the United States does not own. In her colonies of Algiers and Tunis as well as in parts of Morocco are vast deposits. In

America, Florida produces two thirds of the present output, but Tennessee, South Carolina and Montana also yield large amounts. The largest deposit in the world is found in Utah, Montana, Wyoming, and Idaho, where government investigations report at least 2,500,000,000 tons of 30 per cent calcium phosphate in sight.

Exercise 8. — Would you expect to get hydrogen sulfide by treating phosphorus sulfides with dilute acids? Why?

ARSENIC

History. — The alchemists were acquainted with arsenic and even the ancient Greeks knew some of its compounds. Albertus Magnus first prepared the element in the thirteenth century. Brandt (the discoverer of phosphorus) proved "white arsenic" to be a "calx" or ash of the element. After Lavoisier made clear the nature of oxidation this calx was recognized as the oxide.

Occurrence. — Arsenical pyrites or mispickel ($FeAsS$) is abundant, and there are also deposits of the trioxide, orpiment (As_2S_3), realgar (As_2S_2), and arsenides of iron, nickel and cobalt. It occurs in some sulfide ores, such as those of copper, and thus its oxide is found in flue dust from the smelters.

Preparation. — Much arsenic is made commercially by heating arsenical pyrites:

$$4\ FeAsS \rightarrow 4\ FeS + 4\ As.$$

In the laboratory, reduction of the trioxide by hot carbon is an easy method:

$$2\ As_2O_3 + 3\ C \rightarrow 4\ As + 3\ CO_2.$$

Arsenides react with water or, more rapidly, with acids to form arsine. This is similar to the action of nitrides and phosphides on water:

$$Zn_3As_2 + 6\ HCl \rightarrow 2\ AsH_3 + 3\ ZnCl_2.$$

The famous Marsh test for arsenic is based on reduction by nascent hydrogen. A flask (Fig. 71) containing a frothing mixture of pure zinc and sulfuric acid is connected with a glass tube constricted at two points. Through a funnel a solution of the suspected arsenic compound is added. The arsine formed by reduction is heated as it passes through the delivery tube and the element is deposited farther along as a shining mirror. It is best worked so that the mirror forms in a constriction. As little as

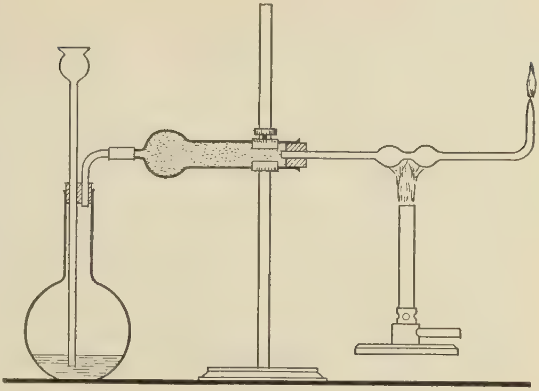


FIG. 71

one millionth of a gram of arsenic can be detected in this way, so it is a famous test in poisoning cases. An interesting variation is to light the hydrogen as it issues from the delivery tip and hold a porcelain dish in the flame. The heat of the flame decomposes arsine in the middle of the jet and a shining black spot of the element forms on the cold dish.

$$2\,AsH_3 \rightarrow 2\,As + 3\,H_2$$

Properties. — In physical properties arsenic resembles the metals, but chemically it is a non-metal, an acid former. Like another member of this group, phosphorus, it exists in allotropic forms.

The common form is gray, brittle, has a specific gravity of 5.727 and volatilizes on heating. (When a solid passes into vapor without melting it is said to sublime.) Like other solids that sublime it can be melted under pressure. Sublimation affords an easy method of purifying. The vapors have a strong garlic odor. The element does not oxidize in cold air, but burns, forming a white smoke of the trioxide.

When the vapors of arsenic are cooled suddenly a yellow modification is secured. Unlike the common form it is soluble in carbon disulfide. Moreover its specific gravity is less, only 4.7.

Where common arsenic is heated suddenly a third form, black, crystalline and shining, is obtained.

Arsenic forms alloys or compounds with the metals, arsenides, similar to nitrides and phosphides. It does not displace hydrogen from acids, but with strong oxidizing acids forms arsenic acid. Hot, it unites with chlorine to form the trichloride.

The element is used commercially in alloys as a hardening agent, notably in lead shot.

Oxides. — The trioxide (As_2O_3), a white powder, is the product of burning arsenic or its compounds. Hence it is found mixed with the flue dust of smelters. In the great copper smelter at Anaconda, Montana, this oxide is precipitated from the flue gases by high potential electric charges (75,000 volts). Enormous quantities are recovered. In 1918 the United States used 6323 tons for insecticides, weed killers, preserving bird skins and furs, and in making opaque glass and enamels. It is an important ally of the farmer and among the cotton growers calcium arsenate is much used in fighting the boll weevil. Paris green is a well-known arsenic compound.

The trioxide reacts to a slight extent with water to form arsenious acid and dissolves in hot water to a noticeable degree.

The pentoxide (As_2O_5) cannot be prepared by burning arsenic in plenty of air (like phosphorous pentoxide) but only by heating arsenic acid. It readily unites with water to form arsenic acid again.

The trioxide, erroneously termed "arsenic" by the public, has often been used as a poison. The antidote is freshly precipitated ferric hydroxide (lime water mixed with ferric chloride is a convenient household source).

In some mountainous districts "arsenic eaters" take as much as four times an ordinary "fatal dose" of the trioxide in order to strengthen their respiration and steady their nerves. The body gradually becomes accustomed to such doses.

Halides. — The chlorides, bromides, and iodides are known only for trivalent arsenic ($AsCl_3$, etc.), but the pentafluoride (AsF_5) exists. The trichloride (formed by union of the hot elements) is a colorless liquid boiling at 130° and fuming in moist air. The similarity to phosphorus trichloride is marked:

$$AsCl_3+3\ H_2O \rightarrow As(OH)_3+3\ HCl.$$

Arsine. — Like the corresponding compound, phosphine, this gas is poisonous, only more so. It does not dissolve in water as does ammonia, nor does it form arsonium salts under any conditions. Arsine is readily formed by the action of nascent hydrogen on arsenic compounds:

$$As_2O_3+12\ H \rightarrow 2\ AsH_3+3\ H_2O.$$

Acids of Arsenic. — As with nitrogen and phosphorus, so here we have two types of acids of arsenic, those of trivalent arsenic and those of pentavalent arsenic. The derivation and naming are similar.

As_2O_3 is the anhydride of arsenious acid (H_3AsO_3) and when dissolved in water is in equilibrium with the acid. That the acid is present in solution is evident from the weakly acid reaction and the formation of arsenites on addition of a base. Both acid and arsenites are good reducing agents.

Arsenic acid (H_3AsO_4) is formed by the oxidation of the trioxide with chlorine water or nitric acid:

$$H_3AsO_3+Cl_2+H_2O \rightarrow 2\ HCl+H_3AsO_4.$$

Exercise 9. — Write the equations representing the action of nitric acid on arsenic trioxide.

Exercise 10. — Go back to the first of this chapter and review the comparison of the acids of nitrogen, phosphorus and arsenic. Show the transformation on heating different arsenates.

Arsenic acid is a moderately strong acid, very soluble in water and ionizing in ways similar to phosphoric acid. Like that acid it yields a yellow precipitate on warming with ammonium molybdate and a white one ($MgNH_4AsO_4$) on treating with magnesia mixture. Its anhydride (As_2O_5) is obtained by heating the acid and on treatment with water this anhydride progressively becomes the meta-arsenic acid, pyroarsenic acid and orthoarsenic acid. The meta and pyro acids change so quickly into the ortho that they have not been isolated:

$$As_2O_5+H_2O \rightarrow 2\ HAsO_3 \quad \text{Meta-arsenic acid}$$

$$2\ HAsO_3+H_2O \rightarrow H_4As_2O_7 \quad \text{Pyroarsenic acid}$$

$$H_4As_2O_7+H_2O \rightarrow 2\ H_3AsO_4 \quad \text{Orthoarsenic acid}$$

Exercise 11. — If you can't isolate meta-arsenic acid, how can you prepare $NaAsO_3$?

Mitscherlich's Law. — In 1819 Mitscherlich observed that corresponding salts such as KH_2PO_4 and KH_2AsO_4 had the same crystalline form or were "isomorphous." Later he made the general statement that "if two substances are isomorphous they must have the same number of atoms similarly arranged in the molecules." This rule during a half century of dispute about valence and atomic weights was of great value in arriving at correct formulas.

The Sulfides. — Solutions of compounds of trivalent arsenic react with hydrogen sulfide to precipitate yellow arsenic trisulfide:

$$2\,AsCl_3 + 3\,H_2S \rightarrow 6\,HCl + As_2S_3.$$

Compounds of pentavalent arsenic react slowly, even when kept almost boiling, to yield yellow arsenic pentasulfide. Both sulfides are oxidized by hot concentrated nitric acid to arsenic acid with release of sulfur. With prolonged action the sulfur may become sulfuric acid.

The sulfides of the sodium group react with arsenic trisulfide to form soluble salts.

The Sulfo Acids and Salts. — On warming arsenic trisulfide with sodium sulfide (ammonium sulfide is often used with similar results) a soluble salt is obtained. If sodium polysulfide (Na_2S_2) be used a different soluble salt is obtained:

$$\left\{\begin{array}{l} As_2S_3 + 3\,Na_2S \rightarrow 2\,Na_3AsS_3, \text{ Sodium sulfarsenite} \\ As_2S_3 + 3\,Na_2S_2 \rightarrow 2\,Na_3AsS_4 + S, \text{ Sodium sulfarsenate} \end{array}\right.$$

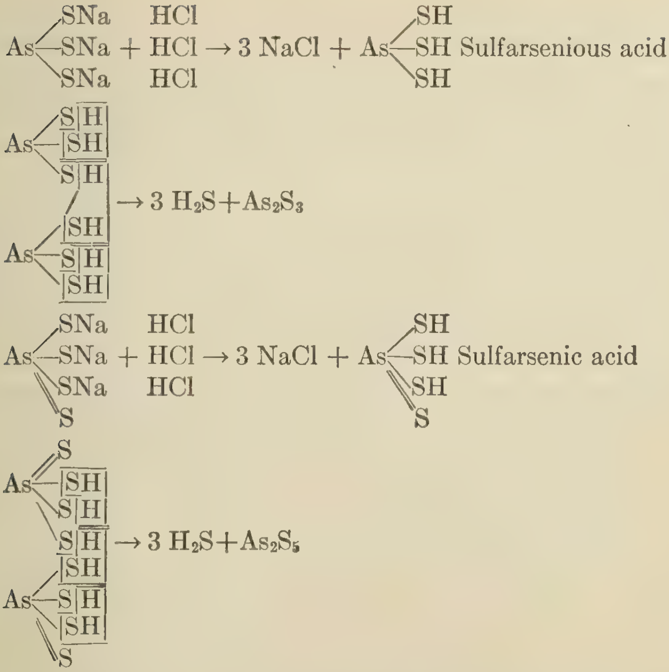
These salts remind us in formula of Na_3AsO_3, sodium arsenite, and Na_3AsO_4, sodium arsenate. The difference is merely in the presence of sulfur in place of oxygen. The name sulfur is then prefixed to the usual name.

In chemistry there are series of sulfur compounds parallel to certain series of oxygen compounds.

COMPARISON OF OXYGEN AND SULFUR COMPOUNDS

Arsenious Acid	H_3AsO_3	Arsenic Acid	H_3AsO_4
Sulfarsenious Acid	H_3AsS_3	Sulfarsenic Acid	H_3AsS_4
Sodium Arsenite	Na_3AsO_3	Sodium Arsenate	Na_3AsO_4
Sodium Sulfarsenite	Na_3AsS_3	Sodium Sulfarsenate	Na_3AsS_4

When these solutions of soluble sulfo-salts are acidified we might expect to get, at least in equilibrium, the free sulfo-acids from which the salts were derived. But precipitates of the sulfides are obtained. The explanation is simple. The sulfo-acids are indeed liberated, but decompose at once with loss of hydrogen sulfide (much like spontaneous loss of water from –OH groups in oxygen acids) and the simple insoluble sulfides are left.



$$As(SNa)_3 + 3\,HCl \rightarrow 3\,NaCl + As(SH)_3$$ Sulfarsenious acid

$$2\,As(SH)_3 \rightarrow 3\,H_2S + As_2S_3$$

$$AsS(SNa)_3 + 3\,HCl \rightarrow 3\,NaCl + AsS(SH)_3$$ Sulfarsenic acid

$$2\,AsS(SH)_3 \rightarrow 3\,H_2S + As_2S_5$$

It is important to note that warming arsenic trisulfide with plain sodium sulfide (Na_2S) does not change the valence of the arsenic, does not oxidize it. But warming with sodium polysulfide (Na_2S_2) gives us a sulfo-salt (Na_3AsS_4) in which the arsenic has a valence of five, and on decomposing this compound with an acid arsenic pentasulfide results. The extra sulfur in the sodium polysulfide simply added on to the arsenic, giving it the full valence of five. These reactions are of the utmost importance in qualitative analysis.

ANTIMONY

History. — Antimony, or perhaps its sulfide, was used as a medicine or cosmetic in the Orient before the Christian era. Basil Valentine, a German monk of the fourteenth century, wrote fully and most reverently of the wonders of antimony. His book, *The Triumphal Chariot of Antimony*, preserved much chemical information. By the close of the eighteenth century the chemistry of antimony was much better known than that of any other element.

Occurrence. — Although found free in small quantities, the element is found chiefly as the sulfide (Sb_2S_3) in China, Japan, Hungary, Bolivia and Mexico. In 1917 the United States imported 17,824 tons of antimony.

Preparation. — The sulfide "stibnite" is often reduced by roasting with scrap iron:

$$Sb_2S_3 + 3\ Fe \rightarrow 3\ FeS + 2\ Sb.$$

By another method the sulfide is melted away from the gangue or common rock in the ore and is then roasted into the oxide and reduced by hot carbon.

Properties. — The change from the non-metallic nature of nitrogen and phosphorus is noticeable in arsenic, but with antimony it becomes decided. This element reacts with sulfuric and nitric acids to form sulfates and nitrates of antimony. Here the element plays the part of a metal. Yet it is unlike the metals in that it is a poor conductor of heat and electricity and its hydroxides are acidic, forming salts with bases.

Antimony is silver-white, brittle, melts at 680° and boils at 1440°. Its specific gravity is 6.7. It expands slightly on cooling from the liquid to the solid state. Only the oxidizing acids attack it and these may form insoluble oxides. In qualitative analysis it is convenient to remember that antimony and tin are the only metals converted into such insoluble oxides by concentrated nitric acid. Antimony reacts readily with phosphorus, arsenic, sulfur and the halogens.

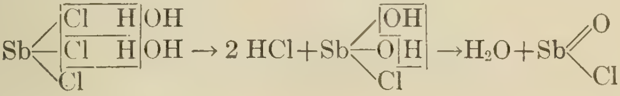
Explosive antimony is a curious modification deposited by electrolysis of a solution of the trichloride in hydrochloric acid. Rubbed in a mortar or heated to 200°, it explodes violently.

Uses. — Its chief value is in making alloys such as type metal, bearing metals and others. Its property of expanding on cooling makes it essential to type metal, for a sharp imprint of the type is desired.

Oxides. — The oxides expected from its similarity to phosphorus occur. Antimony trioxide (Sb_2O_3) is more basic than acidic, but the pentoxide is decidedly acidic. The latter loses oxygen if strongly heated and drops to the lower oxide. A third oxide, (Sb_2O_4), is not of much interest.

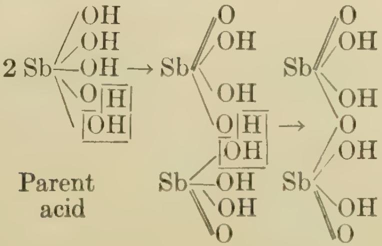
Salts. — Antimony nitrate ($Sb(NO_3)_3$) and the sulfate ($Sb_2(SO_4)_3$) are almost completely hydrolyzed, which shows that the hydroxide of antimony is a very weak base. (See Hydrolysis.) Sodium antimony fluoride ($NaSbF_4$) is very soluble, but is not hydrolyzed because the antimony is in a complex ion. When the trioxide is boiled with potassium hydrogen tartrate ($KHC_4H_4O_6$) tartar emetic is formed. Its formula, $K(SbO)C_4H_4O_6$, shows that one hydrogen of the acid salt is replaced by the antimonyl group (SbO–). Other salts where this group acts like a metal are known. This particular salt is used in medicine and as a mordant in making certain fabrics takes up dyes.

Antimony trichloride ($SbCl_3$), or "butter of antimony," is used to give the dull finish to gun barrels. It is hydrolyzed to the insoluble oxychloride. The basic chloride first formed loses water:

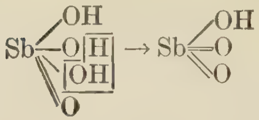


On boiling the chloride is completely hydrolyzed to $Sb(OH)_3$ which loses water and becomes Sb_2O_3.

Acids. — The hydroxide ($Sb(OH)_3$) is amphoteric, reacting with strong bases or with strong acids to form salts. The full hydroxide of pentavalent antimony exists for a brief instant if at all (like the similar compounds of the rest of the group) but the derivative H_3SbO_4 is known and is orthoantimonic acid. It is a weak acid, slightly soluble, and loses water on heating, yielding the pentoxide. At different temperatures the meta and pyro acids are obtained — all similar to those of phosphorus.



Pyroantimonic acid,
$H_4Sb_2O_7$



Metantimonic acid, $HSbO_3$

The potassium pyroantimonate is soluble but the sodium salt is practically the only insoluble salt of sodium and hence is of interest in analysis.

Exercise 12. — How change from KH_2SbO_4 to potassium metantimonate?

Stibine. — Antimony compounds are reduced by nascent hydrogen with formation of the poisonous gas stibine just as arsine is formed. In fact the famous Marsh test for arsenic can be applied to antimony. The antimony spot is blacker than the arsenic spot and is not dissolved by a solution of sodium hypochlorite (unlike arsenic). Arsine reacts with a solution of silver nitrate with formation of black, finely divided silver, but stibine reacts to form silver antimonide ($SbAg_3$).

Sulfides and Sulfo-Salts. — Freshly precipitated antimony trisulfide is orange-red, but when melted it is black like the mineral stibnite:

$$2\,SbCl_3 + 3\,H_2S \rightarrow 6\,HCl + Sb_2S_3.$$

It dissolves in alkaline sulfides like arsenic sulfide. Instead of sulfarsenic acid we refer to sulfantimonic acid, etc. The oxidation relations are the same and spontaneous decomposition of the sulfo-acids with precipitation of simple sulfides follows the same rules. Write all the formulas and reactions that are given under sulfo-compounds of arsenic with the substitution of Sb for As and they will be correct.

BISMUTH

Bismuth has been known for centuries, although for some time confused with antimony. The characteristic properties were discovered by Pott in 1739.

Occurrence. — Bismuth is much scarcer than the other members of the group. The free element is found as well as the sulfide (Bi_2S_3), oxide (Bi_2O_3) and the telluride (Bi_2Te_3). Bolivia is the chief source. In 1918 the United States imported 135,700 pounds.

Preparation. — Roasting the sulfide ore and then reducing the oxides with hot carbon is a common method of preparation.

Properties. — Bismuth is strictly metallic. It is silver-white with a reddish tint, brittle and crystalline. It melts at 269°, boils at 1435° and although stable in air, burns to the trioxide (Bi_2O_3). It unites directly with the halogens and decomposes steam at a red heat.

There is no use for the element alone but in alloys it is rather important. This will be discussed in the topic on Alloys at the end of the chapter.

Compounds. — Bismuth trioxide, Bi_2O_3, is basic, but the other oxides, BiO, Bi_2O_4 and Bi_2O_5, are neither basic nor acidic. The hydroxides are more basic than acidic. The trichloride (by treating bismuth with chlorine or aqua regia) hydrolyzes with precipitation of $BiOCl$. (See the similar compound of antimony.) The nitrate ($Bi(NO_3)_3$) hydrolyzes very noticeably, producing a salt used in medicine under the name "bismuth subnitrate." X-ray pictures of the intestines are made possible by doses of this salt. Sulfur compounds in the intestine change this into the sulfide, which is impermeable to the X-rays and hence appears black on the photograph.

Probably only salts of trivalent bismuth are known. There is no compound similar to arsine. The element is too metallic for its sulfide to dissolve in alkaline sulfides.

Exercise 13. — Suppose you knew only that the chloride of bismuth was 66 per cent bismuth and 37 per cent chlorine and that the specific heat of bismuth was 0.0303. How would you calculate the atomic weight of bismuth and the correct formula for the chloride?

ALLOYS

Centuries ago pure metals were practically unknown. In the metallurgy of copper, for example, other metals present in the ore mixed with the copper to form an alloy. We are told of the "lost art" of hardening copper and yet the explanation is simple. Certain copper ores containing other metals yielded alloys much harder than pure copper. This type of alloying was rather accidental, being done in ignorance. Then metal workers learned that addition of some copper to gold or silver in coins made a product that was much harder, lasted longer. In ancient times copper and zinc were alloyed to form brass and copper with tin to form bronze. Alloys have multiplied greatly, but it is only recently that their preparation and study have become genuinely scientific. Here is a field of dazzling promise, only partly explored as yet.

Alloys are of at least four main types:

1. A solid solution of one metal in another, or in several others.
2. A definite chemical compound of two or more metals.
3. A mixture of such a compound with an excess of either constituent. This means particles of the compound in a matrix of the rest of the material.
4. A mixture of a solid solution with an excess of either constituent. Again we have solid particles (the solid solution) in a matrix of the rest of the material.

Alloys are usually made by melting the constituents together, although there are other ways. On cooling, solid particles of one type may separate from the uniform molten mixture. When a polished surface of such an alloy is etched by a suitable chemical and examined under the microscope, the shape and arrangement of these crystals or aggregates is clearly seen. Such a study is called "metallography."

The "antifriction" or bearing metals which surround revolving shafts are interesting examples of the separation of solid particles in the matrix. These "Babbitts," as they are often called, are alloys of tin and antimony, with some lead and copper. A surface of the harder particles stands the wear and these in turn are supported by a softer matrix into which they sink. In an alloy of a hard matrix and softer separate aggregates scattered through the mass the heat developed by friction is much greater.

The low melting alloys such as Wood's metal or Rose's metal have an important application. The automatic sprinklers dotting the ceilings of great department stores or factories are merely water pipes closed by a plug of such an alloy. When a fire starts these plugs melt very soon and release a spray of water. Wood's metal melts at 60.5°. Solder is another low melting alloy of value. Each metal in the solid solution lowers the melting point or freezing point of the others, hence the mixture melts at a lower temperature than the constituents. This is the same as with salt in water.

The aluminum bronzes (copper and aluminum with possibly a little of some other elements) have a promising future. The alloy has the appearance of gold, yet is hard, machines well, and is not easily corroded. Some recent improvements in the nature of those elements present in very small proportion have given us bronzes that cast sharply and have strength approaching that of steel, which unfortunately does not cast sharply and must be machined at greater expense.

The iron alloys fast becoming of the utmost importance in steel making will be discussed under Iron and Steel.

Amalgams are alloys with mercury as one constituent. Silver amalgam is used in filling teeth.

COMPOSITION AND USES OF ALLOYS[1]

Name	Per cent Composition	Uses
Brass	Cu 73–66 Zn 27–34	Sheets, tubes, cartridges, etc.
Bronze	Cu 88 Sn 8 Zn 2 Pb 2	Strong valves and fittings.
Bronze (aluminum)	Cu 90 Al 10	Hard, noncorrodible, ornamental.
Babbitt metal	Sn 70–90 Sb 7–24 Cu 2–22	Bearings.
Bell metal	Cu 80–75 Sn 20–25	Bells, gongs.
Britannia metal	Sn 95–90 Sb 5–10 Cu 1–3	Cheap table ware.
Chromel (Nichrome)	Ni 60 Cr 40	Resistance wire for electric heating. (Patented.)
Duralumin	Al 95.5 Cu 3.0 Mn 1.0 Mg 0.5	Strongest and best of aluminum alloys. Airplane and auto parts.
Fusible (Wood's)	Bi 38 Pb 31 Sn 15 Cd 16	Automatic sprinklers, fuse plugs.
German silver	Ni 18–25 Zn 20–30 Cu (remainder)	Table ware, cheap jewelry.
Magnalium	Al 90–94 Mg 10–6	Scientific instruments. Balance beams.
Manganese bronze	Cu 56 Zn 41 Sn 0.5 Fe 1.0 Mn 0.5 Al 1.0	Propeller blades, noncorrodible and with great wearing qualities.

---

[1] From *Principles of Metallography* by Williams. Published by McGraw-Hill and Co., New York.

NAME	PER CENT COMPOSITION	USES
Monel metal	Ni 72 Cu 26.5 Fe 1.5	Almost noncorrodible. Propeller blades, wire, sheets, etc.
Pewter	Sn 85–90 Sb 15–10	Platters, bowls, cups, etc. Little used at present.
Solder (soft)	Pb 67 Sn 33	Plumbers' solder.
Steel (low carbon)	C 0.05–0.25 Fe (remainder)	Boiler plate, rivets, sheet, structural work, bridges, shafting.
Steel (medium carbon)	C 0.4–0.8	
Steel (high carbon)	1.2–1.5	Cutlery, rails, wood working tools, drills, castings. Saws, files, razors, ball bearings.
Stellite	Co 80–50 Cr 20–50	Noncorrodible. Used in cutlery, surgical instruments. (Patented.) Fountain pen tips replacing platinum-iridium.
Type metal	Pb 60–85 Sb 8–20 Sn 5–35	

CHAPTER XXI

CARBON

Fully 200,000 compounds of carbon are known (though not by any one man). All other compounds together make up only a small fraction of this impressive number. Carbon chemistry was named Organic Chemistry because it was once thought that only organized living matter could produce carbon compounds. In other words, only plants and animals qualified as synthetic carbon chemists. But since 1827 an infinite number of these compounds have been made in the laboratory.

The importance of carbon and its compounds is evident as we learn that they make up our fuels, whether coal, wood, oil or gas; our lubricants; our foods; our clothing and that they make possible the change from iron to steel. Drugs, dyes, explosives, pencils, printer's ink — these and a host of other necessities are based upon carbon and its compounds.

Since it is found in Group IV, this element has a valence of four as shown by the compounds CH_4, CCl_4, and CO_2. From its location in the middle of the Periodic Table, and at the top of the column, we suspect the truth — its hydroxide (H_2CO_3) is a weak acid and the element is a non-metal. It resembles silicon, tin and lead of the same group in some respects, although not metallic like tin and lead.

The element occurs in nature in two crystalline forms, the diamond and graphite, and is readily prepared from its compounds in such amorphous forms as coke, lampblack, charcoal and boneblack.

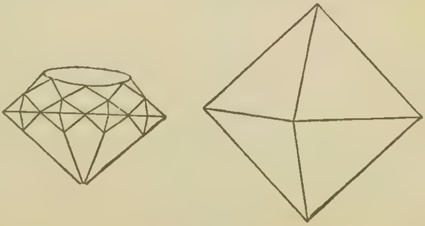


FIG. 72

The Diamond. — The diamond (Fig. 72) is a pure form of carbon crystallizing in the regular system. It is the hardest substance known and hence scratches all other substances. Faulty specimens are used for the cutting edge of rock drills and in the form of dust to polish good diamonds. Its density, 3.5, is greater than that of graphite and the other forms.

About $15,000,000.00 worth of diamonds are mined every year and at that the output is restricted in order to keep up the price. The Kimberley fields of South Africa produce most of these gems although Brazil contributes a good share. The largest diamond ever found, the Cullinan, weighed 3024 carats. Since the carat now equals exactly 0.2 g. this means a crystal of 605 g. or 1.37 pounds. A flaw in the center made it advisable to cut it into smaller perfect gems. One of these weighs 516.5 carats and is the largest cut diamond in the world. The famous Kohinoor of the British crown weighs only 106 carats.

Not all diamonds are colorless, "of the first water." The beautiful Hope diamond is blue, and various other colors are found. When black they are good only for cutting other substances. The cost gives the diamond much of its charm, but it has a real beauty when skillfully cut. This is due largely to its high index of refraction. Rays of light are reflected from the interior surfaces of the facets several times before emerging, hence the flashing play of light.

Chemically the diamond is very inactive. At 800° it burns in oxygen, yielding carbon dioxide. Heated to a high temperature in absence of air it swells up into a sort of coke (once thought to be graphite). It resists the attack of most reagents.

In 1894 Moissan prepared synthetic diamonds, but unfortunately the largest was only half a millimeter in diameter. He dissolved pure carbon (from sugar) in molten iron and suddenly chilled the crucible by dropping it in water or in molten lead. A solid shell instantly formed, but the interior solidified more slowly. As iron expands on solidifying enormous pressure must have been developed. As the carbon, soluble only in very hot iron, came out of solution it crystallized in diamond form. Pressure and high temperature were necessary — the same conditions as those found in the depths of the earth. The iron was dissolved away from the diamonds by acid.

Graphite. — Graphite is a crystalline form of carbon differing noticeably from diamond. It is black, soft, and made up of six-sided leaflets which slide easily over one another. It is lighter than the diamond, having a density of only 2.25. Chemically it is quite inactive, yet it is possible to burn it at very high temperatures.

The most important deposits are in Ceylon, Siberia, Austria and Madagascar, although there are some in Brazil and the United States.

When any form of carbon is heated in the electric furnace it turns into graphite; in fact carbon volatilizes at 3500° without melting and on cooling condenses as graphite. This is the basis of Acheson's method of making artificial graphite at Niagara Falls. A bank of anthracite coal is heaped up and large electrodes inserted at the ends. On passage of a heavy current (40,000 amperes and 200 volts) the heat generated is enough to bring about the desired change. This change is greatly helped by sand or iron oxide which probably form intermediate compounds that decompose, yielding graphite. It was found that the ash of coal furnishes enough of these catalysts. The Acheson process produces over 13,000,000 pounds per year, yet the country uses ten times that amount of graphite, natural and artificial.

Graphite is the essential constituent of lead pencils. Mixed with clay it is molded and baked, and then glued in the groove between two halves of the wooden rod. The harder pencils contain more clay. As a lubricant it is useful where wooden parts rub or where high temperatures or pressures are attained. Acheson prepared a valuable suspension of graphite in water called "aquadag" by the action of tannin as a disintegrating agent. The water merely helps the real lubricant, graphite, to reach all parts of the bearing surface. The same is true of the suspension of graphite in oil called "oil-dag." Acheson remembered the Biblical story of the Israelites who were compelled by the cruel Egyptians to make "bricks without straw." He reasoned that the straw did not act as a mechanical binder but had a chemical action on the clay. This he proved by extracting tannin from straw and then adding the extract to clay. It disintegrated the clay into marvellously fine particles which held together better in making sun-dried bricks. The action of tannin on graphite to form minute particles for better lubrication is a parallel to this.

Graphite is much used as a stove polish to prevent rusting, and in black paints for the same reason, although there is some dispute as to its merits. Since it stands high temperatures, crucibles are made of graphite and clay mixed in the right proportions. Unlike the diamond, graphite conducts electricity well, so a film brushed on any surface, whether wood or wax, makes it possible to suspend the coated object as cathode in a solution of copper sulfate and electroplate a layer of copper on it. This has wide application. In the electrolytic decomposition of sodium chloride, the chlorine released at the anode attacks nearly all substances, so graphite electrodes are preferred because they are not affected.

Amorphous Carbon. — There are several forms of amorphous carbon such as coke, charcoal and soot, but none of these occur in nature. Bituminous coal probably contains little if any free carbon because there are certain liquids which dissolve practically all of a given quantity of coal. At ordinary temperatures there is no solvent for free carbon. These amorphous forms are made by decomposition of carbon compounds as by dry distillation without access of air. The density, hardness and electrical conductivity of all forms of amorphous carbon are increased by high temperature treatment.

Coke. — When bituminous coal is heated in retorts without access of air, many volatile products escape. These include ammonia, illuminating gas and coal tar from the last of which benzene, toluene, phenol (carbolic acid), creosote, naphthalene and many derivatives of great value are secured. Coke is left behind in the retort. It is used in making pig iron from iron ore, in melting metals for foundries, as a domestic fuel and in the manufacture of some carbon compounds. Until the Great War taught us the military and economic value of these by-products, it was our common practice to make coke in the old "beehive" coke ovens, allowing all volatile products to escape into the air. Millions of dollars' worth of these products were lost every year. Now most of our coke is produced in modern by-product ovens that capture everything of value.

Coke burns with almost no flame and no smoke. It is impure carbon since the ash of the coal is still in the coke.

Gas Carbon. — A very dense form of carbon condenses on the walls of retorts in the manufacture of illuminating gas. The prolonged heating to which it was subjected makes it semicrystalline, approximating graphite in properties. It is a fairly good conductor of electricity and so it is ground with coal tar, highly compressed and baked at 1400° for a day or so to make electrodes almost rivaling graphite.

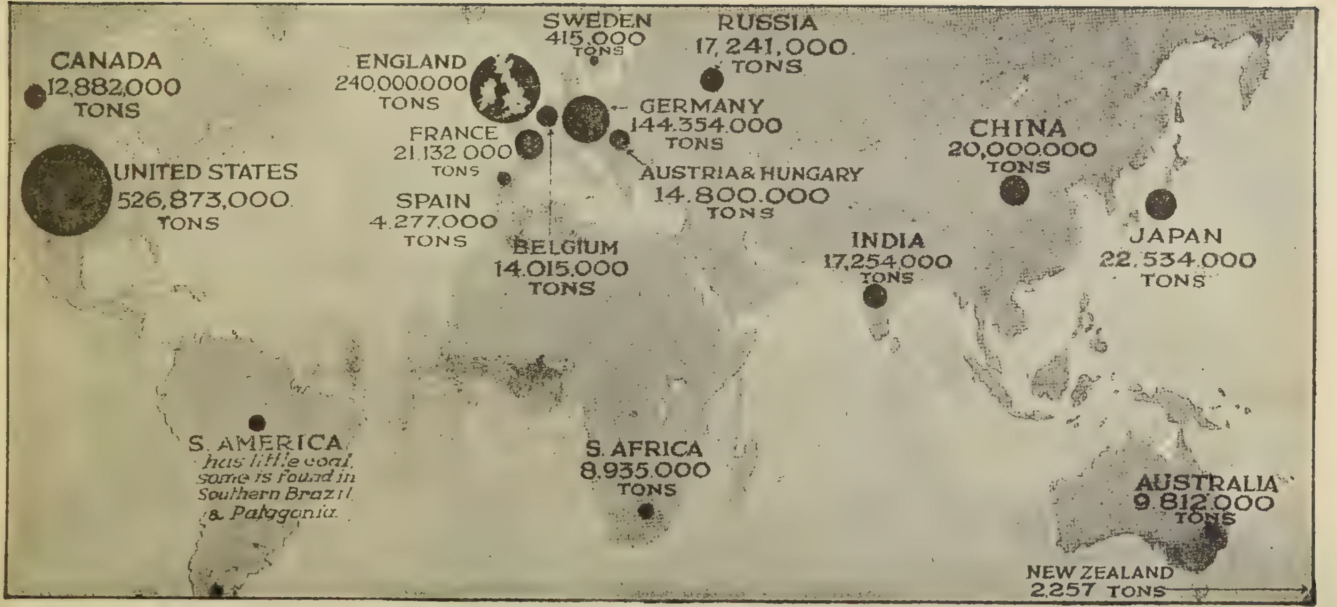
Coal. — The forests of previous ages were buried under deep layers of earth and so subjected to great heat and pressure. This caused a loss of much volatile material and left coal. Peat is a product formed from accumulations of swamp growth. It burns when dry but has a low fuel value. Enormous peat bogs are found in Russia, Ireland, Canada, and the United States.

Lignite, or brown coal, represents an early stage in nature's coal making, hence lignite has only moderate fuel value. Large deposits are found in Arkansas, the Dakotas and other Western states. Bituminous or "soft" coal represents a more advanced stage of coal making in the earth. It yields much volatile matter on distilling and burns with a smoky flame. The fuel value of the best soft coal is high. Anthracite or "hard" coal is almost the final product in coal making. It is older, nearly all volatile matter has been driven off in the depths of the earth, and consequently the anthracite is hard, yields but little volatile matter on destructive distillation, and burns with no smoke and but little flame. Its fuel value is high. (See table on page 310.) The greatest anthracite deposit in the world is found in eastern Pennsylvania. There is a deposit, in Rhode Island, of coal older than anthracite. Nature carried the change beyond anthracite almost into graphite, the end of this series of transformations. As a result it is useless, for it refuses to burn.

The United States is particularly fortunate in its wealth of coal. The world produces about 1,300,000,000 tons annually and of this 40 per cent is mined in this country (Fig. 73). England and Germany follow the United States in coal production. Such deposits act as an industrial and military weapon of the utmost value.

Charcoal. — Wood charcoal was once used in metallurgy in place of the coke of modern times and it is still in some demand. Cheap black gunpowder requires it. Just as coke is the nonvolatile product of coal distillation, so is charcoal the residue remaining when wood is destructively distilled. In earlier days a heap of wood was covered with turf, an opening left for draft, and enough of the wood burned to heat the remainder to the distilling point. This was like the crude method of sulfur refining practiced in Sicily. By modern methods all the volatile products are condensed and used in many important industries. Among these products are wood alcohol, acetone and acetic acid.

Bone charcoal is made by distillation of bones after all the fat has been removed and the bones steamed for glue and gelatine products. This form of carbon contains much calcium phosphate which can be removed by treatment with acid. This boneblack is in great demand by sugar refiners. Solutions of crude cane



Reproduced by permission of *The Sphere*, London.

FIG. 73. — WHERE THE WORLD'S COAL COMES FROM. ANNUAL PRODUCTION

sugar having a slight yellow tint are filtered through a large cylinder containing tons of boneblack. This material, made up of very fine particles, exposes enormous surface to the syrup and holds (adsorbs) the coloring matter of the sugar. The filtrate runs through clear and yields the purest granulated white sugar on evaporation. The adsorptive power of charcoal for various liquids and gases has made it useful in a number of purification processes.

Adsorption (not absorption) is a surface holding and depends largely, but not wholly, on extent of surface. Thus fine powders or very porous material may be expected to show high adsorptive power. A given kind of surface adsorbs some gases, liquids and solids more powerfully than others; in other words, adsorption is selective.

Cocoanut charcoal is one of the most efficient gas adsorbents known. At the temperature of liquid air this form of charcoal adsorbs all gases except hydrogen, helium and neon. This suggests a clever and convenient way of securing a high vacuum. The vessel to be evacuated is sealed to a bulb filled with cocoanut charcoal. On cooling this bulb with liquid air, all the gases present are adsorbed completely. During the Great War the adsorption of poison gases by cocoanut charcoal in the gas mask was the main defense against gas attack. In fact an army without such an adsorbent material could now be demoralized and annihilated with poison gases.

Lampblack. — When a smoky gas or oil flame is chilled by a water-cooled iron pipe, the incandescent carbon of the yellow flame deposits as soot, often called lampblack. It is essential to the manufacture of printer's ink, black paints, and some rubber goods. This is a rather pure carbon and may be further freed from hydrocarbons by strong heating in absence of air.

Physical Properties of Carbon. — Carbon in any form is an odorless and tasteless solid, either colorless as in the diamond, or black as in graphite. The different forms are not of the same density or hardness or electrical conductivity. Exposure of the amorphous forms to intense heat converts them into the graphite modification. Carbon is insoluble in ordinary solvents but is dissolved to a very limited extent by molten iron and a few other metals. Iron takes up 1 or 2 per cent of its weight of carbon which on cooling crystallizes out as graphite. To be exact, only part of it separates. for some carbon reacts with iron to form iron carbide.

Chemical Properties. — Carbon is inactive except when hot. At higher temperatures it unites readily with oxygen to form carbon monoxide and carbon dioxide. It is our most important commercial reducing agent because when hot it removes oxygen from metallic oxides. This is one of the reactions taking place in the blast furnace:

$$Fe_2O_3 + 3\ C \rightarrow 2\ Fe + 3\ CO.$$

With relatively little coke the dioxide escapes, but with an excess coke the carbon monoxide predominates.

Carbon unites with hydrogen to a very limited extent in the electric arc to form acetylene, C_2H_2, but by the catalytic aid of nickel powder at 250° it unites almost completely to form methane (CH_4).

Exercise 1. — This latter reaction is reversible and exothermal. If the materials were heated to 800°, what would the principle of Le Chatelier lead you to expect?

Carbides are compounds of carbon with some of the metals. A carbide of iron is found in steel and has the greatest influence on the properties of the steel. Calcium carbide, CaC_2, which reacts with water to form acetylene, is the product of electric furnace heating of lime and coke. A carbide of silicon called carborundum, SiC, is the most useful abrasive known. Hot carbon also unites with sulfur to form carbon disulfide, CS_2.

Exercise 2. — What mention of calcium carbide was made in the chapter on Nitrogen?

Oxides of Carbon

Carbon Dioxide, CO_2. — Carbon dioxide occurs in the air to the extent of 3 or 4 parts in 10,000 and issues from the earth in a few spots. Some spring waters contain it in solution under pressure. As the water reaches the surface of the earth and the pressure is released the gas escapes with effervescence just as it does in soda water. Its occurrence in the air is due to combustion, the respiration of animals, decay and fermentation. Joseph Black

(1757) first recognized carbon dioxide as a distinct substance. He observed its formation by at least three reactions.

Preparation. — 1. The simplest method of preparation is by direct union of carbon and oxygen. The carbon must be burned with an excess of oxygen or part of the dioxide may be reduced to carbon monoxide by the hot carbon:

$$C+O_2 \rightarrow CO_2,$$
$$CO_2+C \rightarrow 2\,CO.$$

But it is not necessary to burn pure carbon. Any carbon compounds such as coal, wood, paper and oils burn with formation of the dioxide. Any other elements present would probably burn to their oxides.

EXERCISE 3. — Balance the equations: Hot $CH_4+O \rightarrow ?$
Hot $C_2H_5OH+O \rightarrow ?$

The first represents the burning of natural gas and the second the burning of alcohol.

2. High heating of some carbonates (but not of the carbonates of sodium and potassium) yields carbon dioxide. The manufacture of quicklime from limestone in the limekiln depends upon this reaction. In a closed tube this reaction is reversible, but not where the gas is removed:

$$CaCO_3 \rightarrow CaO+CO_2.$$

3. The laboratory method is the treatment of carbonates such as limestone or marble with a dilute acid. A Kipp generator, which allows the acid to touch the carbonate only when the gas is being drawn off, is illustrated in Fig. 74:

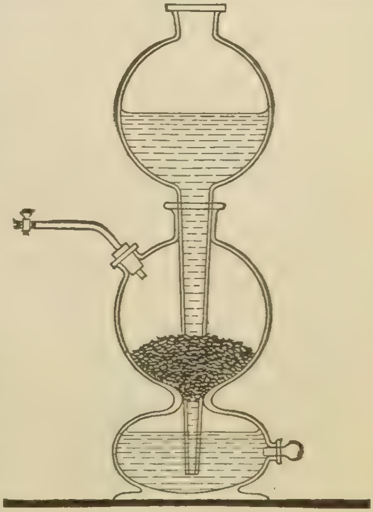


FIG. 74

$$CaCO_3+2\,HCl \rightarrow CaCl_2+H_2CO_3,$$
$$H_2CO_3 \rightarrow H_2O+CO_2.$$

The carbonic acid first formed is very unstable, and decomposes with escape of carbon dioxide.

4. The fermentation of sugar solutions to form alcohol yields carbon dioxide as one product. The froth on "hard" cider indicates the escape of this gas. It is interesting to learn that in 1920 a million dollar company began the commercial capture of carbon dioxide in connection with alcohol distilleries.

Physical Properties. — Carbon dioxide is a colorless, odorless gas, one half heavier than air. At 15° water dissolves its own volume of the gas. The soda water of fountains contains much more in solution under about 10 atmospheres pressure. The solution has a slightly sharp, pungent taste. The gas is sold commercially in thick steel cylinders under 60 atmospheres pressure. Most of it is liquid. The liquid, allowed to escape from the inverted cylinder (Fig. 75), vaporizes so rapidly that it is quickly cooled to −79°, at which temperature it freezes to a snowlike solid. This may be caught in a cloth bag.

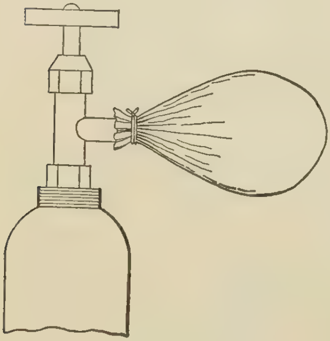


FIG. 75

Some very spectacular experiments may be performed with this snow. Addition of ether to give better contact makes it possible to freeze mercury (−40°). If the mercury be placed in a small pasteboard box and a stick of wood held in it, a hammer is secured with a head of solid mercury. The pasteboard box is readily torn off and nails may be driven into a board with the hammer. A thin piece of beefsteak is "cooked" white and is so brittle it may be broken in pieces. A rubber tube is frozen so that it can be snapped like a pipestem. A rubber stopper thus chilled gives a ringing sound when thrown against a brick wall.

The critical temperature of carbon dioxide is 31.33°. At 20° its vapor pressure is 59 atmospheres.

Chemical Properties. — Carbon dioxide is so stable that its dissociation ($2\,CO_2 \leftrightarrows 2\,CO + O_2$) is only 1.8 per cent at 2000°. For this reason it does not support combustion except for very active elements. Magnesium burns in the dioxide, leaving black carbon. Carbon above 1000° (almost white heat) reduces carbon dioxide to the monoxide:

$$CO_2 + C \rightarrow 2\,CO.$$

In a furnace full of a deep bed of brightly glowing coals the carbon dioxide formed at the bottom of the layer is probably reduced to the monoxide by the upper layers of incandescent coal. The monoxide then burns at the surface with a blue flame.

With metallic oxides carbon dioxide unites to form carbonates:

$$CaO + CO_2 \rightarrow CaCO_3.$$

Quicklime exposed to the air not only takes up moisture but reverts, as indicated by the equation, to calcium carbonate. It is then "air slaked."

Carbonic Acid, H_2CO_3.—Since a water solution of carbon dioxide is weakly acid, there must be a reaction between water and carbon dioxide to form an acid, carbonic acid. On boiling, all the carbon dioxide is removed, so the reaction is evidently reversible:

$$H_2O + CO_2 \leftrightarrows H_2CO_3.$$

The water solution has a pleasantly sharp taste, hence its use as plain soda water. One might realize that the acid is weak by reflecting that the moisture and carbon dioxide of the lungs certainly do not injure the tissues of the lungs as would be the case if carbonic acid were a strong acid. Fortunately only half of one per cent of it is ionized in a 0.01 N solution. One of the hydrogen atoms in each molecule ionizes more readily than the other:

$$H_2CO_3 \leftrightarrows \overset{+}{H} + H\overset{-}{CO_3}.$$

In fact, the further ionization of $H\overset{-}{CO_3}$ is minute:

$$H\overset{-}{CO_3} \leftrightarrows \overset{+}{H} + \overset{--}{CO_3}.$$

Carbonates and Bicarbonates. — Passage of carbon dioxide into a solution of a base yields carbonates or bicarbonates, depending on the relative amounts of carbon dioxide used. The carbonic acid formed is simply neutralized by the base:

$$(1)\ 2\,NaOH + H_2CO_3 \rightarrow 2\,H_2O + Na_2CO_3,$$
$$(2)\ Na_2CO_3 + H_2CO_3 \rightarrow 2\,NaHCO_3$$

Reaction (1) becomes (2) when an excess of carbon dioxide is bubbled through the solution. The difficulty is in knowing when to stop addition of carbon dioxide for reaction (1). If the "normal" salt, Na_2CO_3, is required, a simple device is to divide the given solution of the base into two equal parts, saturate one part with the gas (which insures the formation of the bicarbonate, $NaHCO_3$), and then mix the two solutions. This means the addition of a number of molecules of the base equal to the number of molecules of the bicarbonate:

$$NaOH + NaHCO_3 \rightarrow H_2O + Na_2CO_3.$$

The bicarbonate is really an acid salt, and the few hydrogen ions it yields ($NaHCO_3 \leftrightarrows \overset{+}{Na} + \overset{+}{H} + \overset{--}{CO_3}$) unite with the hydroxyl ions of the base to form water and the ordinary carbonate. Excess of carbon dioxide in soil waters dissolves limestone by formation of the soluble calcium bicarbonate ($CaCO_3 + H_2CO_3 \rightarrow Ca(HCO_3)_2$). The water then becomes "hard."

All carbonates are insoluble except those of the sodium group. Thus an easy way to precipitate the insoluble ones is to add any soluble carbonate to a solution of any salt of the desired metal. This really means bringing together the CO_3 ion (from any soluble carbonate) with the metallic ion (from a solution of any of its salts):

$$BaCl_2 + Na_2CO_3 \rightarrow BaCO_3 + 2\ NaCl,$$

$$\overset{++}{Ba} + \overset{--}{CO_3} \rightarrow BaCO_3.$$

Some carbonates are formed by direct union of carbon dioxide and a metallic oxide:

$$CaO + CO_2 \rightarrow CaCO_3.$$

The normal carbonates of the sodium group are hydrolyzed to very strongly basic solutions (salts of a strong base and a weak acid) while the bicarbonates suffer very little hydrolysis. All bicarbonates decompose on heating into carbonates, water and carbon dioxide:

$$2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

Uses of Carbon Dioxide. — This gas is useful in fire extinguishers, where it is formed when needed by action of sulfuric acid on a dilute solution of sodium bicarbonate (Fig. 76). The Solvay process of making soda requires huge quantities of the gas and much is used in soda water. Carbon dioxide, generated in the dough, is the chief leavening agent used by the baker.

Carbon Monoxide, CO. — This colorless, poisonous, almost odorless gas is formed by burning carbon with an insufficient supply of air:

$$2\,C + O_2 \rightarrow 2\,CO.$$

Stoves too closely damped may allow escape of some of this dangerous gas into the house. The blue flame flickering over a bed of red hot coals is due to the final burning of carbon monoxide into the dioxide. The dioxide formed in the lower layers is reduced by the hot carbon above. Access of air to the surface of the fuel completes the combustion.

$$CO_2 + C \rightarrow 2\,CO.$$

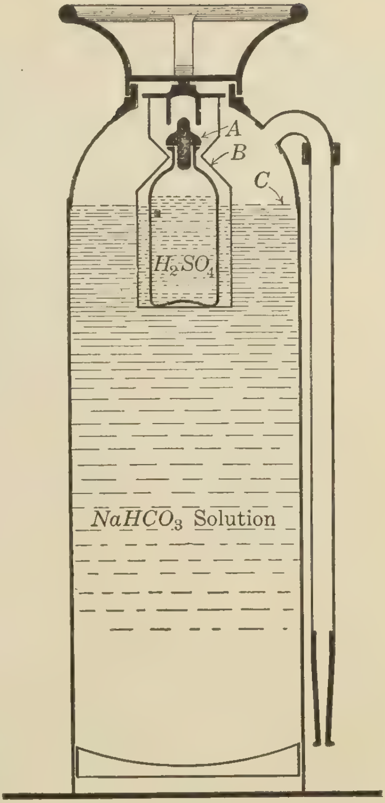
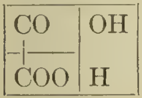


FIG. 76

A convenient laboratory method of preparation of the monoxide is to heat oxalic acid crystals with concentrated sulfuric acid, which merely extracts the elements of water. This removal of some of the atoms from each molecule causes a general collapse. Among the fragments are carbon monoxide and dioxide. Bubbling the mixture of the two gases through a solution of sodium hydroxide removes the dioxide. (Why?)



$$\left|\begin{array}{l|l} CO & OH \\ \hline COO & H \end{array}\right| \rightarrow CO + CO_2 + H_2O \text{ (taken by the sulfuric acid).}$$

A better laboratory method of making carbon monoxide is to allow formic acid to drop slowly into concentrated sulfuric acid. Formic acid loses the elements of water to the concentrated sulfuric acid:

$$HCOOH \rightarrow H_2O + CO.$$

Great care must be used in working with carbon monoxide. Alexander Smith states that 1 vol. in 800 vol. of air is fatal if breathed for 30 minutes. It was planned to equip our gas masks in the war with a mixture able to oxidize the monoxide into the harmless dioxide. Carbon monoxide is absorbed (by reaction) by a mixture of solutions of cuprous chloride and ammonia. The monoxide is a good reducing agent, extracting oxygen from hot metallic oxides:

$$(1)\quad CuO + CO \rightarrow Cu + CO_2,$$
$$(2)\quad Fe_2O_3 + 3\,CO \rightarrow 2\,Fe + 3\,CO_2.$$

Reaction (2) is a most important step in the extraction of iron from its ores in the blast furnace. The monoxide unites with sulfur and also with some hot metals, especially nickel and iron. When chlorine and the monoxide are passed over animal charcoal (as a catalyst) in the sunlight, the famous poison gas, *phosgene* or carbonyl chloride, is formed:

$$CO + Cl_2 \rightarrow COCl_2.$$

The Cycle of Carbon in Nature. — All the vast amount of carbon dioxide thrown into the atmosphere by processes of combustion, of decay, fermentation, and animal respiration, is taken up by plants as a valuable food. In the sunlight chlorophyll, the green coloring matter of leaves, is formed and this catalyzes the following reaction:

$$6\,CO_2 + 5\,H_2O \rightarrow C_6H_{10}O_5 + 6\,O_2.$$

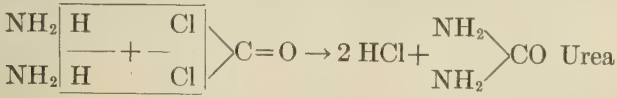
This $C_6H_{10}O_5$ is starch, or cellulose, with molecules containing a large multiple of this formula. The admirable perfection of nature's work is evident from the equation. Not only do plants purify the air but they return all the oxygen of the carbon dioxide to the free atmosphere as oxygen. The woody material of plants actually comes from the air and the water of the sap. When this wood is burned or decays or the starchy foods are eaten, all the carbon dioxide given off makes the same cycle.

EXERCISE 4.— Diagram the Carbon Cycle (see Nitrogen Cycle on page 220).

Phosgene, $COCl_2$. — This dangerous gas has been mentioned under Carbon Monoxide. It is a colorless liquid below 8°:

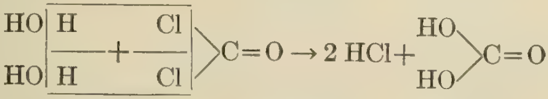
$$CO + Cl_2 \rightarrow COCl_2.$$

Although used as one of the most effective "war gases" it can also be made the starting point in the manufacture of valuable dyes. Its relation to urea is interesting. Direct reaction with ammonia forms urea, identical with that dissolved in the urine:



$$\begin{matrix}NH_2\\NH_2\end{matrix}\left|\begin{array}{c}H \qquad Cl\\ \overline{\quad}+\overline{\quad}\\ H \qquad Cl\end{array}\right|\!>C=O \rightarrow 2\,HCl+\begin{matrix}NH_2\\NH_2\end{matrix}\!>CO \text{ Urea}$$

With water, phosgene reacts (hydrolysis) to form carbonic acid and hydrochloric acid.



$$\begin{matrix}HO\\HO\end{matrix}\left|\begin{array}{c}H \qquad Cl\\ \overline{\quad}+\overline{\quad}\\ H \qquad Cl\end{array}\right|\!>C=O \rightarrow 2\,HCl+\begin{matrix}HO\\HO\end{matrix}\!>C=O$$

Exercise 5. — What relation has urea to the cycle of nitrogen in nature?

Carbon Tetrachloride, CCl_4. — This is a colorless liquid (boiling at 77°). It is made commercially by passing dry chlorine into carbon disulfide in the presence of a little iodine as catalyst:

$$CS_2+3\,Cl_2 \rightarrow S_2Cl_2+CCl_4.$$

The less volatile sulfur monochloride is left behind on distilling off the carbon tetrachloride. The latter, being noninflammable, is much used as a fire extinguisher. The Pyrene cylinders so necessary in homes and laboratories contain this liquid. Carbon tetrachloride is also a safe solvent for fats, oils and greases. "Carbona," used in cleaning grease spots from clothing, contains enough of it to make the mixture safe.

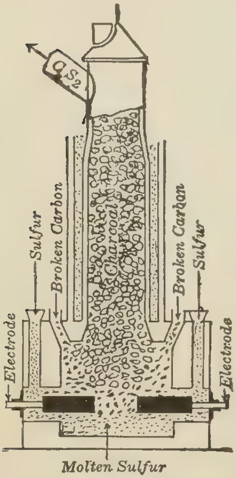
Exercise 6. — Of what commercial value is sulfur monochloride? (See chapter on Sulfur.)

Exercise 7. — Starting with free carbon how could you make carbon tetrachloride?

Carbon Disulfide, CS_2. — Carbon disulfide is a volatile, inflammable liquid. It has no odor when pure, but certain impurities give it a very unpleasant odor. It is a very heavy liquid and possesses a high index of refraction. The manufacture is simple. Charcoal and sulfur are fed into an electric furnace (Fig. 77) and react in absence of air. (Why absence of air?) The carbon disulfide vapor is condensed as it leaves the furnace:

$$C+2\,S \rightarrow CS_2.$$

As a solvent for rubber, sulfur, iodine and other substances, it has value. Much of it is used in killing rats, mice, ants and prairie dogs. A little poured into an obnoxious ant hill will be found very effective. Since it is highly inflammable, caution must be used when the liquid is applied in buildings. It is dangerous because it vaporizes at low temperature and the vapors form an explosive mixture with air.



By permission from Black and Conant's *Practical Chemistry*, The Macmillan Co.

FIG. 77

Calcium Carbide, CaC_2. — Calcium carbide is prepared in the electric furnace from lime and coke:

$$CaO + 3\ C \rightarrow CaC_2 + CO.$$

It looks like a porous gray stone, but possesses the valuable property of reacting with water to form acetylene gas:

$$CaC_2 + 2\ H_2O \rightarrow C_2H_2 + Ca(OH)_2.$$

Calcium carbide is of very great consequence already and bids fair to multiply its usefulness many times. As the starting point for the manufacture of calcium cyanamide, which itself is a valuable fertilizer and a source of ammonia, nitric acid and explosives, we already know of its economic and military importance. Acetylene will be discussed later and interesting possibilities in its development will be pointed out. Robert Hare, a brilliant pioneer among American chemists, really made the first electric furnace the world ever saw (although unfortunately not much of the world saw his work). With this furnace he made the first calcium carbide, but the world gave little attention to it. Although this was well over a century ago, this substance was forgotten until the Cowles Electric Smelting and Aluminum Company of Cleveland in 1885 made some by accident and observed that when moistened an inflammable gas (acetylene) was given off. Later the Canadian chemist, Thomas Willson, put calcium carbide on the list of important commercial products.

Carborundum, SiC. — The Cowles Company in 1885 also prepared carborundum in their electric furnace but did not understand what the product really was. Acheson, of graphite fame, deserves the credit of "discovering" the substance in 1891. His first device for electric heating of clay and charcoal was crude, but he secured beautiful blue and black iridescent crystals which he was able to sell as "gems" at \$560 a pound. Soon he made them in ten ton batches — and the price fell. A bank of coke and sand which furnish the essential elements is built up with sawdust, to make the mass porous, and salt, to make it fusible. On passage of a heavy electric current through the mass, the heat of resistance brings about the desired reaction (Fig. 78):

$$3\ C + SiO_2 \rightarrow SiC + 2\ CO.$$

Only the diamond is harder than carborundum, so this compound is the greatest abrasive known. Pulverized and mixed with clay or other material as a binder, it is shaped into cutting wheels and whetstones and then baked to harden the binder. Machine shops sharpen tools by its aid with greater speed than when emery is used. Carborundum is decomposed at 2220° and is attacked by alkalies.

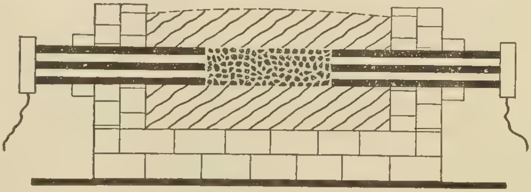


FIG. 78

Cyanogen, the Cyanides, and Cyanates. — Cyanogen is a very poisonous gas which can be made, in small quantities, from carbon and nitrogen in the electric arc. It is better prepared by heating mercuric cyanide:

$$Hg(CN)_2 \rightarrow Hg + C_2N_2.$$

Heated with potassium at high temperatures, it forms potassium cyanide, KCN. This is a white solid prepared commercially by other methods. All the cyanides are deadly poisons and their acid, HCN, "prussic acid," is a colorless volatile liquid of the greatest toxic power. The cyanides of sodium and potassium are used in analysis and in some industries. They are soluble in water and are hydrolyzed with basic reaction since they are derived from an extremely weak acid.

Heated with a solid oxidizing agent, the cyanides of sodium or potassium yield cyanates:

$$2\ NaCN + O_2 \rightarrow 2\ NaCNO.$$

Ammonium cyanate is of historic interest because in 1828 the German chemist Wohler heated its solution, and to his astonishment found that its atoms were rearranged to form urea, the first "organic" compound ever prepared without the "life process." Since ammonium cyanate and urea have the same atoms and the same number of them they are said to be "isomers." The difference is only in the arrangements of these atoms within the molecules:

$$NH_4CNO \rightarrow (NH_2)_2CO.$$

Exercise 8. — What connection has the Bucher process with cyanides?

CHAPTER XXII

THE HYDROCARBONS

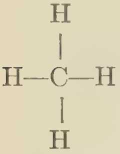
Homologous Series. — There are several hundred hydrocarbons (compounds of hydrogen and carbon), most of them found in petroleum, natural gas, asphalt, and coal tar products. These are divided into a few series, with some very definite relationships between the members.

Methane Series C_nH_{2n+2}		Ethylene Series C_nH_{2n}		Acetylene Series C_nH_{2n-2}		Benzene Series C_nH_{2n-6}	
Methane	CH_4			(Ethine or)			
Ethane	C_2H_6	Ethylene	C_2H_4	Acetylene	C_2H_2		
Propane	C_3H_8	Propylene	C_3H_6	Propine	C_3H_4		
Butane	C_4H_{10}	Butylene	C_4H_8	Butine	C_4H_6		
Pentane	C_5H_{12}	Pentylene	C_5H_{10}	Pentine	C_5H_8		
Hexane	C_6H_{14}	Hexylene	C_6H_{12}	Hexine	C_6H_{10}	C_6H_6	Benzene
Heptane	C_7H_{16}	Heptalene	C_7H_{14}	Heptine	C_7H_{12}	C_7H_8	Toluene
Octane, etc.	C_8H_{18}	Octalene	C_8H_{16}	Octine	C_8H_{14}	C_8H_{10}	Xylene

In each series any one member differs from its neighbor by one carbon and two hydrogens (CH_2). This regular progression in molecular weight is the reason for the name, "homologous series." The general formula for the series is useful. For example, in the methane series (so called from the name of its simplest member) we know that a hydrocarbon with five carbons must have twelve hydrogens in the molecule (C_5H_{12}) because in the series formula (C_nH_{2n+2}), the n is 5 in this case and $2n+2=12$.

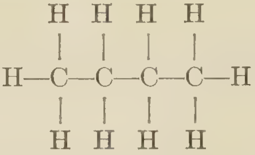
The methane and benzene series are by far the most important. The entire methane series up to a molecule of 60 carbon atoms is found in petroleum. The first member makes up over 90 per cent of natural gas. The first four members are gases at ordinary temperatures: from C_5H_{12} to $C_{15}H_{32}$ they are liquids and from $C_{16}H_{34}$ up they are solids.

The existence of so many compounds of two elements depends wholly on the tetravalence of carbon and the ability of carbon atoms to hold other carbon atoms in long chains or rings.



$$\begin{array}{ccccc} & & H & & \\ & & | & & \\ H & - & C & - & H \\ & & | & & \\ & & H & & \end{array}$$

and



$$\begin{array}{ccccccccccc} & & H & & H & & H & & H & & \\ & & | & & | & & | & & | & & \\ H & - & C & - & C & - & C & - & C & - & H \\ & & | & & | & & | & & | & & \\ & & H & & H & & H & & H & & \end{array}$$

illustrate this. Name them.

Methane. — Methane is formed when many kinds of organic matter are heated out of contact with air. Thus the gases from the distillation of coal and wood contain it. Inflammable bubbles may be stirred up from marshy pools where decaying vegetation has formed methane or "marsh gas." It is often found in coal mines, where it is known as "fire damp," and is thus the cause of dangerous explosions. Petroleum contains some of this substance, but the chief source is natural gas, which may contain 90 to 95 per cent of methane.

It is a colorless, odorless gas, inflammable, insoluble in water and is rather indifferent chemically. Yet chlorine, in the sunlight, slowly replaces its hydrogen. The critical temperature of methane is so low ($-82°$) that even at great depths in the earth it is not liquefied.

Methane can be made directly from its elements by heating carbon and hydrogen together to 250° in the presence of finely divided nickel as a catalyst. In the laboratory it is often prepared by distilling dry sodium acetate with sodium hydroxide:

$$CH_3COONa + NaOH \rightarrow Na_2CO_3 + CH_4.$$

Aluminum carbide moistened with water (or better, dilute acid) yields methane in a way that led Mendeleeff to believe that carbides deep in the earth were the sources of natural gas:

$$Al_4C_3 + 12\ H_2O \rightarrow 4\ Al(OH)_3 + 3\ CH_4.$$

Exercise 1. — How would you make aluminum carbide, reasoning from the preparation of calcium carbide?

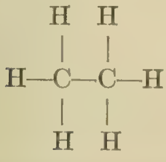
Natural gas is a valuable fuel, yielding carbon dioxide and water on combustion. When 1000 cubic feet of the gas burns, over 10 gallons of water could be collected by chilling the vapors. Natural gas and oil occur in the same fields and, in fact, the gas is really the volatile part of the oil deposit. The great gas fields of Pennsylvania, West Virginia, Ohio and Indiana have wasted most of their resources and thus a great national asset will soon be exhausted. It is the pressure of reservoirs of this gas that forces oil out in "gushers."

In recent years much "high test" gasoline has been extracted from natural gas by pressure and condensation methods or by dissolving the gasoline vapor in heavy oils. This very volatile "casing head" gasoline is blended with heavier gasolines to make a good motor fuel. In 1918 over 90,000,000 gallons were saved in this way.

It is possible to make many valuable derivatives from methane, as will be shown in the next chapter.

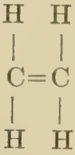
Exercise 2. — How many grams of oxygen are required to burn 100 liters of methane, both gases being measured under standard conditions?

Ethylene, C_2H_4. — This colorless, inflammable gas burns with a luminous flame due to the separation of much incandescent carbon. To its presence is due much of the illuminating power of some commercial gases. It is the first member of a series of unsaturated hydrocarbons. In methane, carbon has its full valence of four, but in ethylene, C_2H_4, the two carbons use only a valence of three each. In the structural formula this unsaturated condition may be represented by a double linkage between the carbons. This means only the kind of unsaturation existing in ethylene.



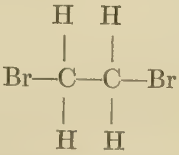
$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ H- & C & - & C & -H \\ & | & & | & \\ & H & & H & \end{array}$$

Ethane (saturated)



$$\begin{array}{ccc} H & & H \\ | & & | \\ C & = & C \\ | & & | \\ H & & H \end{array}$$

Ethylene (unsaturated)



$$\begin{array}{ccccc} & H & & H & \\ & | & & | & \\ Br- & C & - & C & -Br \\ & | & & | & \\ & H & & H & \end{array}$$

Ethylene bromide (saturated)

As a result of its unsaturation, this compound has an ability to add on bromine and other elements until the usual valence of four is exercised by the carbon. A common laboratory experiment is to pass ethylene gas into bromine, securing the heavy, colorless liquid, ethylene bromide, $C_2H_4Br_2$. Ethylene itself may be made from alcohol by heating with concentrated sulfuric acid. The effect of the reaction is removal of the elements of water from the alcohol:

$$C_2H_5OH \rightarrow H_2O + C_2H_4.$$

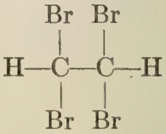
When any saturated hydrocarbon is heated strongly some ethylene is produced. Even methane can be made to yield it:

$$2\,CH_4 \rightarrow 2\,H_2 + C_2H_4.$$

Acetylene, C_2H_2. — This gas has a lower percentage of hydrogen even than ethylene, so it is still more unsaturated. Each carbon is able to add on two bromine atoms or other atoms and become saturated with the usual four valences. The structural formula represents the linkage between the carbons by three bonds, but this is only to be counted as representing the particular degree of unsaturation existing in acetylene:

$$H—C\equiv C—H$$

Acetylene
(unsaturated)



$$\begin{array}{ccccccc} & & Br & & Br & & \\ & & | & & | & & \\ H & — & C & — & C & — & H \\ & & | & & | & & \\ & & Br & & Br & & \end{array}$$

Acetylene bromide
(saturated)

The formation of the gas by addition of water to calcium carbide has been given previously ($CaC_2 + 2\,H_2O \rightarrow Ca(OH)_2 + C_2H_2$). A very little is formed in the carbon arc when hydrogen is present. When ethylene is passed through very hot tubes some acetylene is formed:

$$C_2H_4 \rightarrow C_2H_2 + H_2.$$

The negative heat of formation of acetylene is so large (–53,200 cal.), that on burning all this heat is liberated as well as that due to the combustion of carbon and hydrogen. When one gram-molecular weight burns the total heat liberated is 303,760 cal.

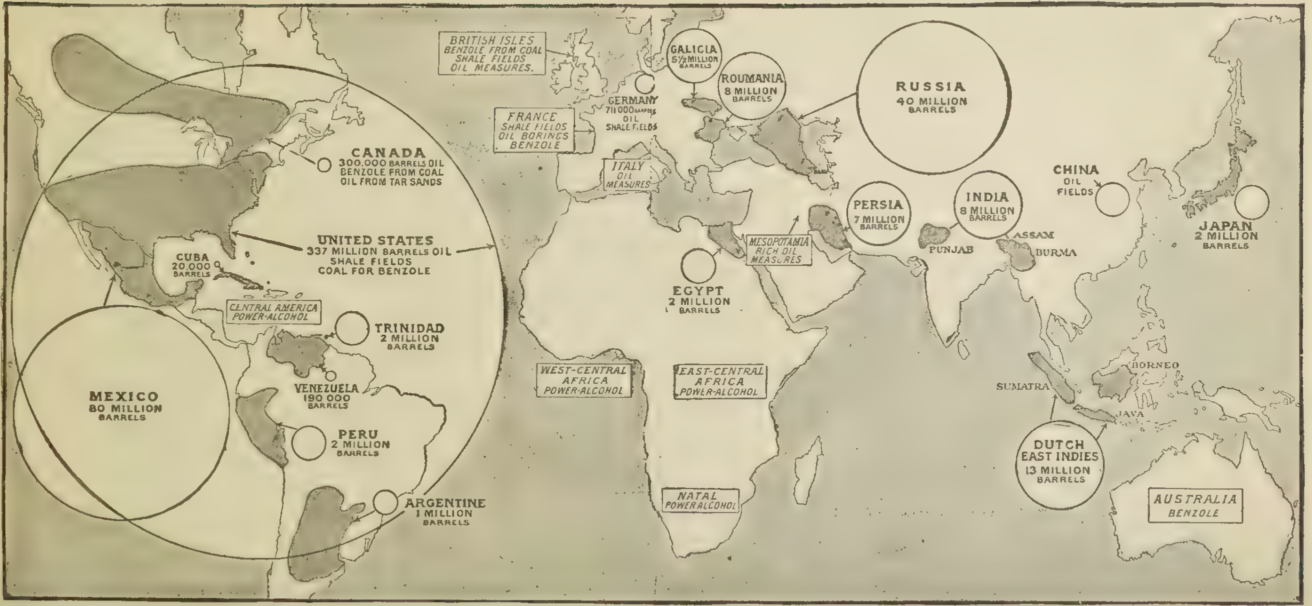
Heat of decomposition of C_2H_2			53,200 cal.
Heat of combustion of $2\,C=$	$(2\times12\times8040)$	$=$	192,960 cal.
Heat of combustion of $2\,H=$	$(2\times28,800)$	$=$	57,600 cal.
	Total		303,760 cal.

Burned in a special burner a very white flame is secured if plenty of air is admitted, otherwise a smoky flame results. Fed with oxygen in the acetylene torch, an intensely hot flame is obtained. With this a 6-inch steel shaft can be cut through in less than a minute and heavy plates cut with equal speed. It is an interesting fact that acetylene can't be compressed in supply cylinders without great danger of a violent explosion (due to its endothermic nature), but it can be dissolved safely in acetone under pressure and so handled. The "Prestolite" cylinders once used so much for lighting automobiles were prepared on this principle. Ethylene has been proposed as a substitute for acetylene since it can be compressed safely.

Isoprene, C_5H_8, a member of another unsaturated series, has been heated with sodium or concentrated hydrochloric acid to form artificial rubber. Unfortunately this process is not yet on a commercial basis.

Petroleum. — Petroleum is a mixture of hydrocarbons of the methane series varying in color from a light greenish-yellow to a green or reddish-brown. It is sometimes limpid but usually rather thick. Theories of its origin vary. Decomposition of animal or plant material deep in the earth probably account for its occurrence. The United States produces two thirds of the world's petroleum, with Russia second. In recent years Mexico has become a very great producer (Fig. 79). Lesser but important deposits are found in Roumania, Galicia, India, Japan, and Persia. Herodotus writes of this oil as known to the Persians in 450 B.C. but there was no particular use for it until it occurred to Col. Drake in 1859 to drill a well near Oil City, Pennsylvania. Some of the Russian "gushers" have yielded 200,000 barrels a day while the gas pressure was high. The Pennsylvania field has now declined to a small percentage of our national production and the leadership has been taken by California with the Texas-Louisiana field second. Kansas and Oklahoma produce well and send much of their oil over a thousand miles through 6-inch pipes to refineries near New York City. The total production of the United States in 1920 was 442,163,000 barrels.

Refining crude petroleum is essentially the separation by distillation of the more volatile from the less volatile constituents. The crude oil is heated by direct flame in huge steel cylinders. At first, the very volatile fractions including gasoline come off and are separated for further treatment. As the temperature rises the kerosene fractions (still higher boiling point) come off and later the heavier lubricating oils. The various fractions are distilled again, some of them with steam and finally the liquids



Reproduced by permission of *The Sphere*, London.

FIG. 79. — THE WORLD'S OIL FIELDS. ANNUAL PRODUCTION

listed below are secured. Pentane is the only member of the methane series mixture that can be isolated readily. The other distillates are mixtures of two or more hydrocarbons. The term *benzene* is used rather loosely. A list of the fractions follows:

NAME	COMPONENTS	BOILING POINT	USES
Petroleum ether	Pentane-hexane	40°– 70°	Solvent-gas-making.
Gasoline	Hexane-heptane	70°– 90°	Solvent, motor fuel.
Naphtha	Heptane-octane	80°–120°	Solvent, fuel.
Benzine	Octane-nonane	120°–150°	Solvent.
Kerosene	Decane-hexadecane	150°–300°	Illuminating oil.
Middle fractions (gas oil)			To "crack" into more gasoline or to enrich water gas.
Lubricating oils			Lubrication.
Vaseline Paraffin			Candles, sealing jellies, water-proofing.
Tar residue			Artificial asphalt.

Paraffin is not a solid residue left after everything else has been distilled off, but is crystallized from the lubricating fractions by chilling. Vaseline or petrolatum is prepared from the heavy distillates.

The "cracking" of the middle fractions is a very recent development of tremendous importance.[1] This distillate had little use previous to 1913 when Burton discovered that oils heated to 340°–450° C. at four or five atmospheres pressure yielded gasoline where there was none before. The hydrocarbons decompose and some of the new combinations are in the form of gasoline molecules. To be exact, this general principle was known earlier, but Burton applied it successfully, and his process is the only one operating on a large scale. Rittman's method of cracking petroleum differs somewhat and gives promise of future success.

Burton's discovery (1913) came just in time to save the Allies in the Great War. This was so much a war of auto transportation of men and supplies to the front lines that there was never enough gasoline motor fuel for the pressing military needs. But here was a creation of new gasoline in great quantity in addition to the amount naturally occurring in the petroleum. Before protesting about the price of gasoline, motorists may reflect that but for the large scale development of the cracking process, prices would be still higher and there would not be enough gasoline to supply the demand. Several million barrels of gasoline are now being made each year by the Burton process.

---

[1] There is an excellent article on the cracking of petroleum in *Jour. Chem. and Met. Eng.* *23*, 908, 1920.

Of course kerosene in the United States is no longer the leading fraction in distillation. It is really of minor importance since electric lighting has so largely supplanted kerosene lamps. Farm tractors are using some of this kerosene as a motor fuel because of its relative cheapness.

The threatened exhaustion of oil deposits in the not very distant future is alarming from the standpoint of lubrication. Modern machinery makes enormous demands on special oils for the different lubrication needs. Control of the world's great oil fields is a prize that nations will strive for. Steamships and battle cruisers are finding crude oil or waste refinery fractions an ideal fuel. The liquid fuel is atomized by air or steam and burned under the boilers as a spray. The gain in speed, cruising radius and saving in labor is vital. No wonder Great Britain, with her vast navy, worked hard to get a grip on the Mexican oil fields. It is said she already controls more oil fields than do all other nations. Mexican and other high sulfur oils in the crude state will probably furnish the fuel oil of the future.

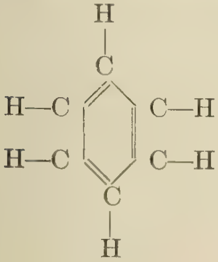
Asphalt was, doubtless, formed by further chemical changes in petroleum. A great lake of it occurs in the island of Trinidad and small deposits in several of our states. Its use in surfacing streets is well known.

Benzene and its Series, C_6H_6. — Benzene was discovered in 1825 by Faraday and about twenty years later was found by A. W. Hofmann in the gases distilled from coal tar. It is a colorless liquid, lighter than water and insoluble in water, of a slight odor (not unpleasant), melting at 6°, boiling at 80.4°. It burns with a smoky flame and is an excellent solvent for grease, resins and rubber. It has long been used in paint and varnish removers and in the manufacture of artificial leather.

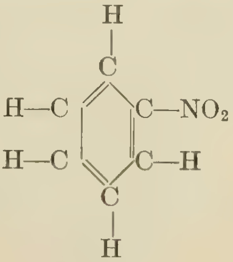
Chemically benzene must be classed as an unsaturated hydrocarbon, since it is capable of adding on six hydrogen atoms or six bromine atoms per molecule. It reacts with nitric acid to form nitrobenzene, $C_6H_5NO_2$, and this in turn is reduced by nascent hydrogen to aniline, $C_6H_5NH_2$, the mother substance of a host of beautiful "aniline dyes." It can also be attacked by hot concentrated sulfuric acid and other reagents. In fact over one half of all carbon compounds are derivatives of benzene:

$$C_6H_6 + HNO_3 \rightarrow C_6H_5NO_2 + H_2O,$$
$$C_6H_5NO_2 + 3\ H_2 \rightarrow C_6H_5NH_2 + 2\ H_2O.$$

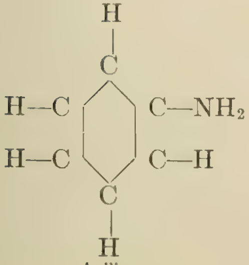
A very interesting line of evidence shows us that the six atoms of benzene are tied together in a ring, very different from the chains of carbons in the methane series. A comparison of a few structural formulas of benzene and its derivatives will be worth while.



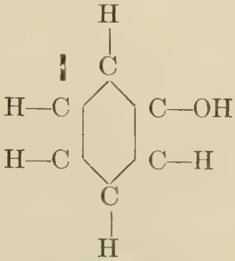
Benzene



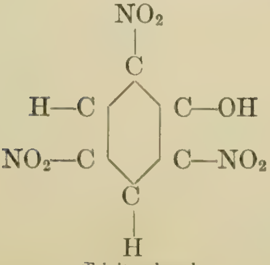
Nitrobenzene



Aniline



Phenol
(Carbolic Acid)



Trinitrophenol
(Picric Acid)

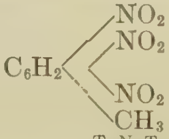
It is sometimes carelessly stated that benzene (with toluene) is obtained by distilling coal tar, itself produced by distillation of coal. But the fact is that very little benzene and toluene are distilled from the tar. The gases from the coal retorts are scrubbed by a spray of some heavy oil which dissolves benzene and toluene. From this solution they are later removed by distillation. During the Great War the demand for benzene as a source of the high explosive, picric acid, was great and only exceeded by the demand for toluene as a source of "T. N. T." (trinitrotoluene). Naturally the prices soared and the by-product coke oven industry grew by leaps and bounds. But even in peace times great quantities of benzene will be in demand, if not as the starting point in making dyes, drugs, and photographic chemicals, then as a motor fuel. By a slight adjustment of the carbureter, benzene (or benzol as the public insists on calling it) yields more power in the engine than does gasoline. Already it is in very extensive and rapidly growing use for this purpose. The United States could produce 100,000,000 gallons a year without increase in the tonnage of coke, but even this much would not be enough. Our motors now use 1,000,000,000 gallons of gasoline a year.

Toluene, C_7H_8. — This colorless liquid, boiling at 110°, is closely associated with benzene in manufacture from bituminous coal and closely resembles benzene in many properties. Its special interest to the public is as the source of the world's greatest explosive, "T. N. T." (trinitrotoluene). Toluene differs from benzene by having a methyl group ($-CH_3$) in place of one hydrogen atom. On treatment with concentrated nitric acid and sulfuric acid three nitro groups ($-NO_2$) are introduced in place of three more ring hydrogen atoms:

$$C_6H_5.CH_3 + 3\ HNO_3 \rightarrow 3\ H_2O + C_6H_2(CH_3)\ (NO_2)_3.$$

C_6H_6
Benzene

$C_6H_5.CH_3$
Toluene



$$C_6H_2\left\langle\begin{matrix}NO_2\\NO_2\\NO_2\\CH_3\end{matrix}\right.$$

T. N. T.

Coal Tar. — The distillation of bituminous coal has often been mentioned in this text, especially in connection with ammonia and benzene. Until recent years coke was produced in "beehive" ovens without capturing any of the gaseous products. But war prices of ammonia, benzene, toluene, phenol and the dyes led to a very rapid expansion of the by-product coke oven industry. The most modern ovens consist of banks of narrow brick chambers each about 40 feet long, 10 feet high and 1.5 feet wide. Each chamber holds 12–16 tons of bituminous coal. The ovens are separated by a series of vertical flues in which gas is burned to furnish the heat for coking.

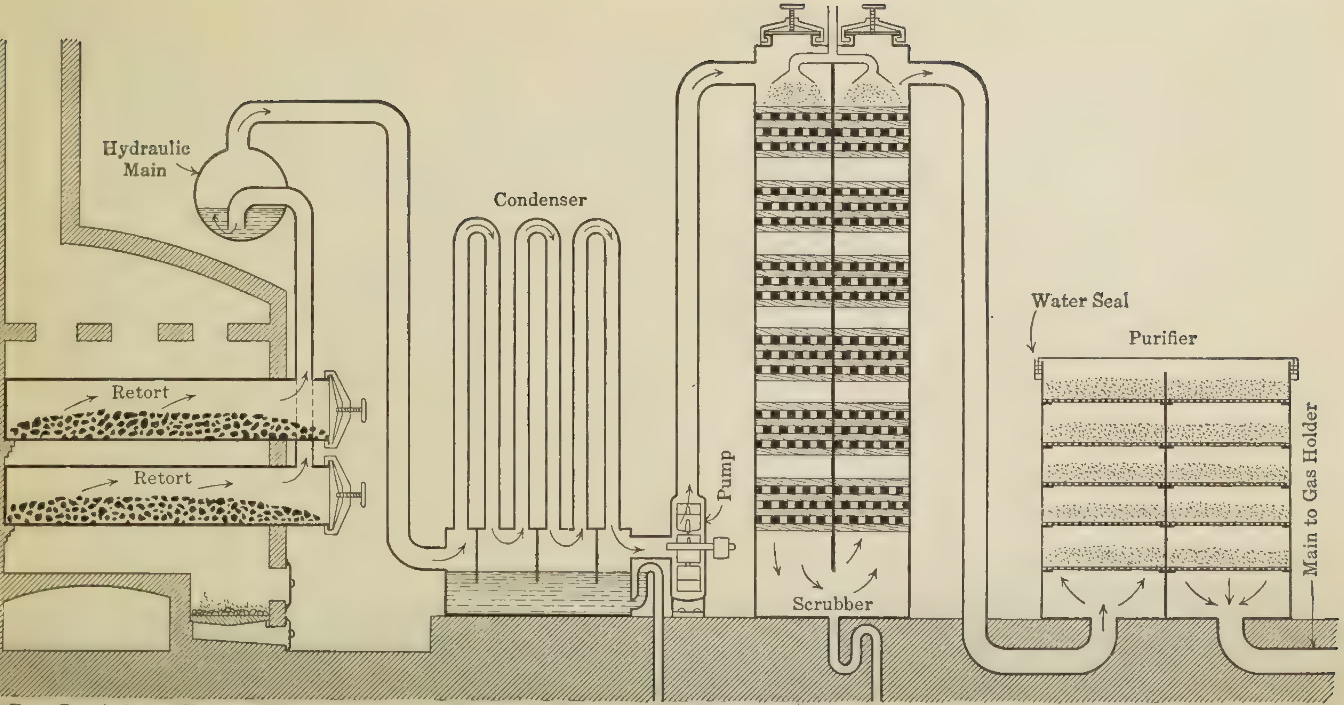
The volatile products are washed with water to catch ammonia and some tar and with heavy oil to catch most of the benzene and toluene. The tar is condensed and the remaining coal gas finally purified for use as a fuel. Coal tar is a black, disagreeable mass, but from it are made the most delicate colors the world ever saw and some of the most beneficial medicines as well as dainty perfumes. The blackness is due to free carbon. This tar was once used only for making roofing paper or felt and has been burned as a fuel, but now the demand for its fractions is large. On redistilling the tar the following products, given in order of volatility, are obtained:

1. Light oil containing a small part of the benzene and toluene.
2. Middle oil containing phenol (carbolic acid).
3. Heavy oil containing creosote.
4. Anthracene oil.
5. Residue of pitch.

The middle oil yields carbolic acid used as a disinfectant and as a source of the explosive, picric acid. Naphthalene (moth ball material) is also taken from this fraction. It was used as the starting point in making artificial indigo.

The heavy oil or creosote is in great demand as a wood preservative. Each year 100,000,000 gallons are used and yet less than one third the railroad ties of this country are creosote dipped. From the anthracene of the next fraction is made alizarin, a most important dye, once obtained only from the madder plant. The pitch left in the still has extensive use in the manufacture of roofing paper, surfacing of roads, filling between the blocks in paving and in coating iron pipes. If heated long enough, hard pitch results, and this may be used as a pulverized fuel low in ash and sulfur.

It is estimated that in 1918 fully 45 per cent of our 60,000,000-ton production of coke was made in by-product ovens, while in



From *Foundations of Chemistry*, Blanchard and Wade. Copyright. By arrangement with American Book Company, Publishers.

FIG. 80. — COAL GAS

1913 only 27 per cent was so made. By-product ammonia was equivalent to 450,000 tons of ammonium sulfate in 1918. All these products taken together were worth $200,000,000.

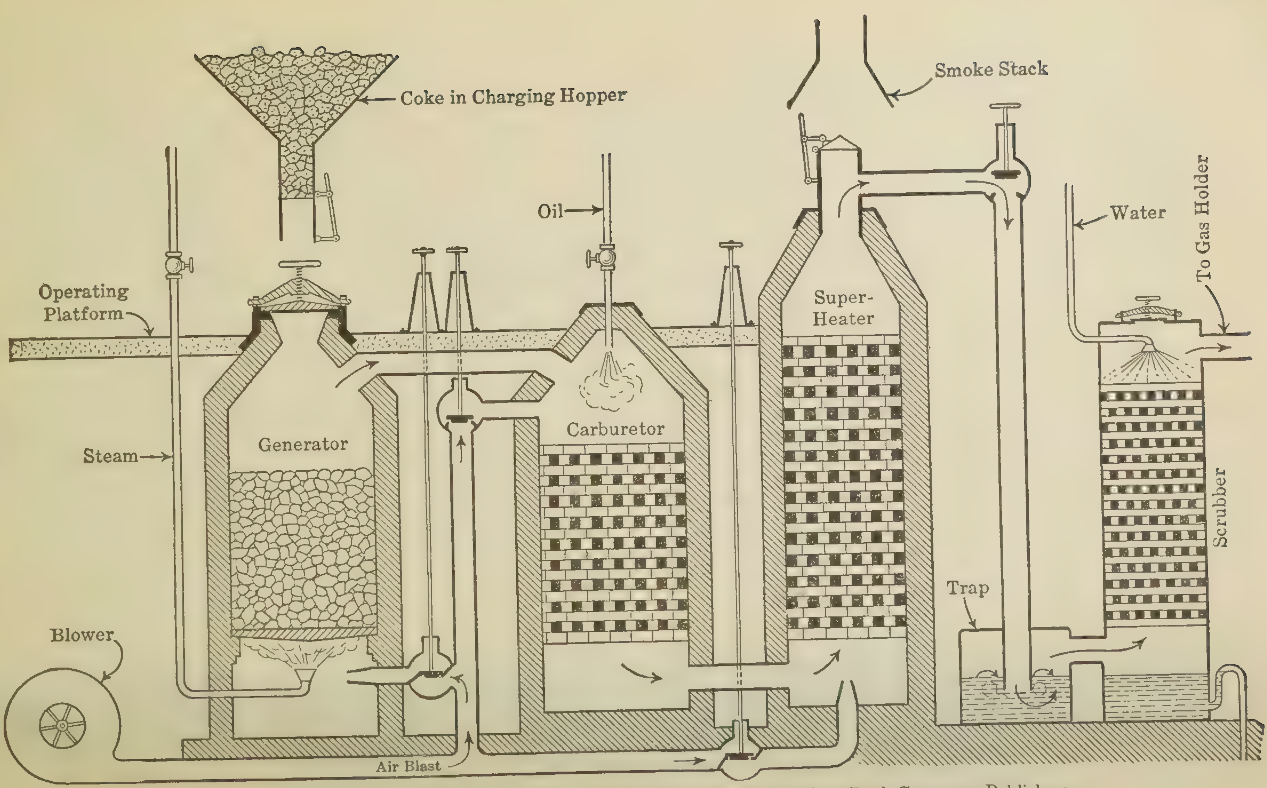
Coal Gas. — This most volatile fraction of the distillation of "soft" coal is a valuable fuel. It is largely hydrogen and methane with a little ethylene, benzene, etc. Its composition varies with the coal and the temperature and the rapidity of coking (Fig. 80). Higher temperatures favor decomposition of the hydrocarbons, increasing the percentage of hydrogen and reducing the illuminating power, but greatly increasing the volume of gas. Nearly half this gas is used to heat the retorts, but where the local market justifies it, the cheaper producer gas may be used for retort heating, thus releasing the entire output of coal gas for the market.

One ton coal	Gas, 12,000 cu. ft.	Benzene, 10–20 lbs. (largely washed out of the gas). Toluene, 3 lbs. Xylene, 1.5 lbs.
	Ammonium sulfate, 7–25 lbs.	
	Tar, 120 lbs.	Phenol, 0.5 lb. Naphthalene, 0.27 lb. Anthracene, 0.25 lb. Pitch, 80 lbs.
	Coke, 1200–1500 lbs.	

Water Gas. — Water gas is prepared by burning coke with a forced draft of air until the bed of coke is almost white-hot (Fig. 81). Of course the carbon dioxide formed is a waste. Next, the air is shut off and steam forced through the coke for five or six minutes. At about 1000° the reaction proceeds, but when the coke falls much below this temperature the reaction stops. The steam is then shut off and air turned on until the coke is again nearly white-hot. The generation of water gas is intermittent:

$$C+H_2O \rightarrow CO+H_2.$$

This gas is much used for domestic cooking and lighting by cities, although coal gas is rapidly gaining in competition. Water gas has good heating value, but is useless for lighting purposes unless used in connection with Welsbach mantles, because the flame is nearly colorless. Some states require a certain candle power of public gases and hence the present custom is to pass the gas through a cylinder containing hot brickwork on which a cheap petroleum oil is sprayed. The mixture then goes to a "super-



From *Foundations of Chemistry*, Blanchard and Wade. Copyright. By arrangement with American Book Company, Publishers.

FIG. 81. — WATER GAS

heater" of similar design, where the brickwork is hot enough to "crack" the saturated hydrocarbons of the enriching oil. Thus the unsaturated ethylene and acetylene are formed and they confer high illuminating value on the lean gas. Methane and other hydrocarbons are also added by this process. Water gas is extremely poisonous before burning, due to its carbon monoxide content, so small leaks in flexible gas tube connections are dangerous. Why are its products of combustion nonpoisonous?

Producer Gas. — In a bed of coal five or six feet deep, the lower layers may be red-hot while the upper layers are not burning at all, possibly only suffering distillation of their volatile matter. If no flame plays over the surface, the escaping gas has good fuel value. Carbon dioxide formed in the lower layers is reduced by the excess of hot carbon above, to the valuable carbon monoxide. All the nitrogen of the air used is found in the producer gas, making up nearly half its volume, hence the heating value is low — but the cost is also low. The best economy is to use this gas while it is still hot, thus saving all its sensible heat. In other words, it does not pay to pipe it to a distance. Even lignite can be converted into producer gas.

A "semi-water gas" is now made by blowing some steam with the air through the deep fuel bed in the producer gas process (Fig. 82). Reaction with the steam adds hydrogen and more carbon monoxide. It is claimed that by the use of producer gas in a gas engine much more power can be obtained from a ton of coal than by burning the coal under a boiler and securing power from the steam generator.

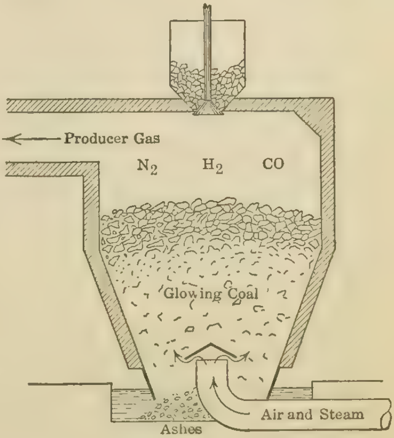


FIG. 82

Blast Furnace Gas. — This is a sort of producer gas taken from the top of a blast furnace in iron making. Here we have a blast of air rising through a deep bed of coke and iron oxide. The product is a mixture of nitrogen, carbon dioxide and carbon monoxide. About one fourth of the mixture has fuel value and is used in the plant to operate gas engines.

Oil Gas. — Petroleum distillates may be "cracked" to form fuel and illuminating gases. Such products are known as "Pintsch gas," "blau gas," etc. Railway trains have been lighted by cylinders of compressed Pintsch gas.

COMPARISON OF INDUSTRIAL GASES

		COAL GAS	ENRICHED WATER GAS	PRODUCER GAS	BLAST FURNACE GAS	OIL GAS
Hydrogen,	H_2	49.8%	37.7%	13.2%	3.5%	13.5%
Methane,	CH_4	29.5	10.0	4.0	0.2	46.5
Ethane,	C_2H_6	3.2	3.2			3.9
Ethylene, etc.	C_2H_4	4.0	13.3			31.3
Carbon monoxide,	CO	8.5	30.4	25.3	26.5	2.4
Carbon dioxide,	CO_2	1.6	3.0	5.4	12.8	0.3
Nitrogen,	N_2	3.2	2.1	55.2	56.9	1.1

FUEL VALUES IN BRITISH THERMAL UNITS

Best bituminous coal	14,000 per pound
Anthracite coal	14,400 per pound
Lignite coal	8000–11,000 per pound
Coke	14,000 per pound
Coal Gas	600 per thousand cubic feet
Enriched water gas	500–600 per thousand cubic feet
Producer gas	145 per thousand cubic feet
Oil gas	300 per thousand cubic feet
Fuel oil	19,800 per pound

A "B. T. U." is the amount of heat necessary to raise one pound of water 1° F.

Flames. — The shape of a flame is determined by the boundary between two gases which are reacting with evolution of light and heat. It does not matter whether a jet of hydrogen burns in an atmosphere of oxygen or a jet of oxygen burns in an atmosphere of hydrogen. The shape of the flame and the products are the same. It may be objected that solids also burn, but when flame is produced, as with wood or coal, it will be found that inflammable gases are distilling from the solid. Thus the flame of a candle is a gas flame. At the tip of the ordinary kerosene lampwick the heat of the flame distills the liquid into gas. Products of combustion may be solids, as with burning iron; liquids, as with burning hydrogen (after cooling); or gases, as with carbon monoxide.

A simple two-zone flame results when such a gas as hydrogen or carbon monoxide burns in air. The inner zone is of unburned gas and the outer zone is the burning zone. But with hydrocarbons flames of at least three zones result. This is to be expected when we remember that hydrocarbons are "cracked" by heat. There must be a zone of decomposition into ethylene, hydrogen, etc. This may be illustrated by using a Bunsen burner with air inlets open; the inner bluish-green cone, *A*, is sharply defined. With less air admitted a luminous cone, *B*, envelops this, while surrounding both is a sheath of perfectly burned gases, *C*, almost invisible (Fig. 83).

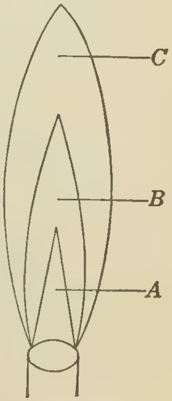


FIG. 83

Smithells made clear that in *A* there is a little burning of the gas, as some carbon monoxide is present there, but cracking of the hydrocarbons into ethylene, acetylene and hydrogen also occurs. In *B* (luminous cone) the carbon monoxide and hydrogen are burned, while the ethylene and acetylene are cracked into hydrogen plus carbon. It is largely due to the incandescence of this free carbon that the flame is luminous. A cold dish pressed into this zone becomes coated with carbon, since the carbon is cooled below its kindling temperature. The student should recall similar experiments with the flames of hydrogen sulfide, arsine and stibine. (What were they?) Finally the hydrogen and carbon are completely burned in the outer sheath *C*.

The luminosity cannot be due wholly to incandescent carbon, as the ammonia flame is luminous. Admission of oxygen at the base of the burner makes the flame nonluminous, but nitrogen or carbon dioxide may be substituted for the oxygen at this point with similar results. Luminosity is also affected by concentration, therefore pressure, and the temperature of the gases *before* burning.

There is a small cone of unburned gas at the tip of the burner and a match head may be held in this without ignition (Fig. 84). A tube of small bore and about 8 cm. long may be inserted into

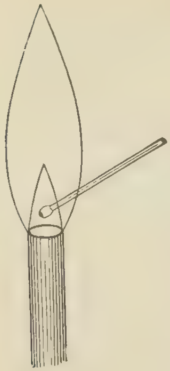


Fig. 84

this zone. The gas tapped off burns at the end of the tube if ignited.

The hottest parts of a flame are just above the tip of *B* and about the middle of the outer sheath. Here the Bunsen flame reaches 1560° or 1570°. At the top of the burner the temperature is only 300°. When too much air is admitted to the base of the Bunsen burner the "ignition wave" sometimes travels downward faster than the gas flows upward. The result is the flame *strikes back* and burns down in the Bunsen tube with unpleasant odor and decided heating of the metal. The Meker burner prevents this by a heavy metal grid on top which cools any ignition wave so that the flame cannot run down the tube. Consequently much air may be admitted at the base and hotter flames obtained (as high as 1775°).

Safety Lamp. — The principle of the Meker grid (Fig. 85) can be shown by thrusting a wire gauze halfway down on a flame (Fig. 86). No flame appears above the gauze simply because the gas was thus cooled below its ignition temperature. The gas passing through the gauze can be ignited by a match. Sir Humphry Davy in 1815 surrounded the coal miner's lamp with a heavy gauze and thus made it safe to carry such a lamp into coal mines containing fire damp (methane). Any methane diffusing through the gauze burns on the inside of the cage, but not on the outside, as the gauze chills the gas below its ignition point.

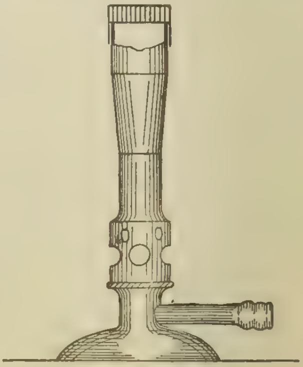


Fig. 85

Welsbach Mantles. — These fabrics, containing 99 per cent thorium oxide and 1 per cent cerium oxide, become incandescent at a comparatively low temperature, so any moderately hot flame inside such a mantle produces intense light, several times as much as if the same gas were burned in an open jet, the old-fashioned way.

Oxidizing and Reducing Flames. — Just below the luminous tip in a flame there is much hot hydrogen and carbon monoxide, both reducing gases. Consequently metallic oxides held in this part of the flame are reduced. At the apex of the flame there are no reducing gases but plenty of hot oxygen, hence the effect of this spot is to oxidize substances held there. A perfectly regulated blue flame has little reducing power at any point.

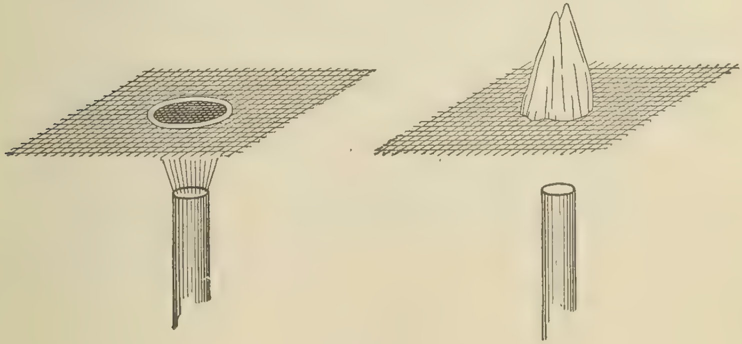


Fig. 86

Flame Colors. — Flames may be colored green, crimson, yellow, etc., by volatilizing in them certain metallic salts, preferably chlorides, since they are the most volatile of all salts.

Exercise 3. — What are the natural sources of hydrocarbons?

Exercise 4. — Can we make hydrocarbons?

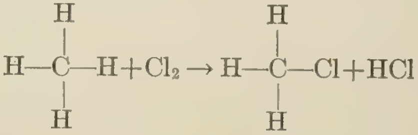
Exercise 5. — Why not use coal tar as a fuel?

Exercise 6. — If a gas containing some sulfur compounds were burned, would the products of combustion be unsafe in the house? Why?

CHAPTER XXIII

DERIVATIVES OF THE HYDROCARBONS

Methane slowly reacts with chlorine, first one atom of hydrogen being replaced by chlorine and, with longer treatment, all four hydrogen atoms being replaced.



$$\mathrm{H{-}\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}{-}H+Cl_2 \rightarrow H{-}\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}{-}Cl+HCl}$$

$$CH_4+Cl_2 \rightarrow HCl+CH_3Cl\text{, methyl chloride}$$
$$CH_3Cl+Cl_2 \rightarrow HCl+CH_2Cl_2\text{, methylene chloride}$$
$$CH_2Cl_2+Cl_2 \rightarrow HCl+CHCl_3\text{, chloroform}$$
$$CHCl_3+Cl_2 \rightarrow HCl+CCl_4\text{, carbon tetrachloride}$$

Ethane reacts with chlorine in the same way:

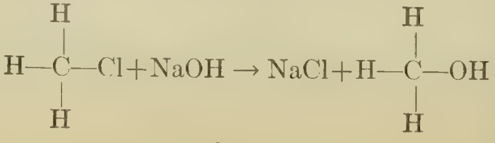
$$C_2H_6+Cl_2 \rightarrow HCl+C_2H_5Cl\text{, ethyl chloride.}$$

It will be noted that a new group is found in methyl chloride, the univalent ***methyl*** group (CH_3). Also in ethyl chloride is found the univalent ***ethyl*** group (C_2H_5). Chloroform and carbon tetrachloride are not made commercially by the above methods, but they may be so prepared.

Starting with methyl chloride (which does not ionize as does sodium chloride), we can make ***methyl alcohol*** very simply (but not profitably). ***Ethyl alcohol*** can be formed in a similar manner:

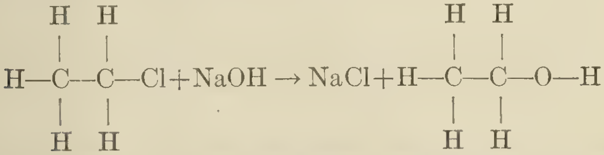
$$CH_3Cl+NaOH \rightarrow NaCl+CH_3OH,$$
$$C_2H_5Cl+NaOH \rightarrow NaCl+C_2H_5OH.$$

As it happens there are better methods of preparing these important and famous (or infamous) alcohols, but this one is valuable in showing us the structure of alcohols.



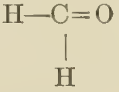
$$\mathrm{H{-}\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}{-}Cl+NaOH \rightarrow NaCl+H{-}\underset{H}{\overset{H}{\overset{|}{\underset{|}{C}}}}{-}OH}$$

Knowing the structure of methane to begin with, the structure given for methyl chloride follows, and hence we are positive that in methyl alcohol the hydroxyl radical must be attached directly to the same carbon atom that holds the other hydrogen atoms. By the same logic we are confident that the structural formulas given in the following equation are correct:

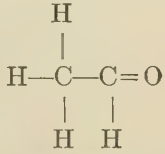


$$\mathrm{H{-}\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}{-}\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}{-}Cl+NaOH \rightarrow NaCl+H{-}\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}{-}\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}{-}O{-}H}$$

Having learned the general structure of alcohols, we can now proceed to show what will happen if we oxidize them (as with sodium dichromate and sulfuric acid):



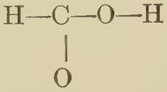
$$\mathrm{CH_3OH+O \rightarrow H.CHO} \quad \text{Structure,}\ \mathrm{H{-}\underset{\substack{|\\H}}{C}{=}O}$$



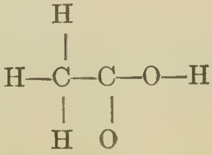
$$\mathrm{C_2H_5OH+O \rightarrow CH_3CHO} \quad \text{Structure,}\ \mathrm{H{-}\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}{-}\underset{\substack{|\\H}}{C}{=}O}$$

Thus we see that two hydrogen atoms are removed from each molecule of an alcohol yielding as oxidation products, ***aldehydes***, the first being formaldehyde, H.CHO, and the second, acetaldehyde, CH_3.CHO. In each, and indeed in all aldehydes, the same group (–CHO) is found, so if "R" stands for any radical, CH_3– or C_2H_5–, etc., we might clearly represent any aldehyde as R.CHO.

Oxidizing alcohols more vigorously, or oxidizing the aldehydes, produces another familiar class of compounds, the ***organic acids.***



$$\mathrm{CH_3OH+O_2 \rightarrow H.COOH} \quad \text{Structure,}\ \mathrm{H{-}\underset{\substack{|\\O}}{C}{-}O{-}H}$$



$$\mathrm{C_2H_5OH+O_2 \rightarrow CH_3.COOH} \ \text{Structure,}\ \mathrm{H{-}\underset{\substack{|\\H}}{\overset{\substack{H\\|}}{C}}{-}\underset{\substack{|\\O}}{C}{-}O{-}H}$$

The first is formic acid, H.COOH, and the second is acetic acid, $CH_3.COOH$. In all organic acids we find the same carboxyl group (–COOH). An important point to remember is that in these acids it is only the hydrogen atom in each carboxyl group that ionizes. The hydrogen atoms in the radicals never ionize. This is why the formula for acetic acid is so often written $H.C_2H_3O_2$, setting apart the ionizable hydrogen. However we prefer to use its halfway structural formula, $CH_3.COOH$.

There are homologous series of all these derivatives, but a study of the first two in each series is all that is necessary for most of us. The same principles usually apply to the higher members of the series. The CH_2 difference between successive members holds throughout.

CHLORINE DERIVATIVES	ALCOHOLS	ALDEHYDES	ACIDS
Methyl chloride, CH_3Cl	Methyl alcohol, CH_3OH	Formaldehyde, H.CHO	Formic acid, H.COOH
Ethyl chloride, C_2H_5Cl	Ethyl alcohol, C_2H_5OH	Acetaldehyde, $CH_3.CHO$	Acetic acid, $CH_3.COOH$
Propyl chloride, C_3H_7Cl	Propyl alcohol, C_3H_7OH	Propylaldehyde, $C_2H_5.CHO$	Propionic acid, C_2H_5COOH
Butyl chloride, C_4H_9Cl	Butyl alcohol, C_4H_9OH	Butylaldehyde, C_3H_7CHO	Butyric acid, $C_3H_7.COOH$
R.Cl	R.OH	R.CHO	R.COOH

EXERCISE 1. — Start with propane and show, step by step, how to make an acid from it. Give the exact structure of each compound.

The Alcohols. — The alcohols remind us of inorganic bases in their structure but not in their action:

$$(1)\ C_2H_5Br + KOH \rightarrow KBr + C_2H_5OH,$$

$$(2)\ NH_4Br + KOH \rightarrow KBr + NH_4OH.$$

There is a good deal of similarity between the above reactions, but there is this fundamental difference. Reaction (2) is between ions, but ethyl bromide (C_2H_5Br) does not ionize, so it reacts as a molecule. When the products are examined it is found that the ethyl hydroxide or ethyl alcohol does not affect litmus paper, does not conduct electricity and, in short, does not ionize at all. It appears, then, that a hydroxyl group attached directly to a hydrocarbon radical has very different properties (alcoholic) from a hydroxyl group attached directly to a metal or even to a non-metal. Any simple alcohol may be represented by the general formula R.OH, where "R" is CH_3, C_2H_5, etc.

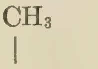
Methyl Alcohol (Methanol), CH_3OH.—In commercial practice this alcohol is made by the retort distillation of wood, hence its common name, "wood alcohol." The distillation of wood to yield charcoal parallels the distillation of coal to yield coke. As with coal the volatile by-products were wasted in former years, but now they are in great demand. Acetic acid and acetone are among the products of wood distillation.

Methyl alcohol (CH_3OH) is a colorless liquid boiling at 67.4°, miscible with water in all proportions, intoxicating and extremely poisonous. Blindness is a common result of a methyl alcohol debauch. In fact, continued exposure to its vapor or contact with the skin is detrimental. Since it is used to "denature" ordinary grain alcohol, there is a real danger in failure to remember the poisonous properties of methyl alcohol. Wood alcohol is much used as a solvent in varnishes and as the starting point in the manufacture of formaldehyde.

Ethyl Alcohol (Ethanol), C_2H_5OH.— Ethyl alcohol (C_2H_5OH), commonly known as "grain alcohol," is a colorless, inflammable liquid boiling at 78° and is miscible with water in all proportions. It is not poisonous, although when taken to excess in strong beverages the effect on the system is distinctly injurious. Like fire, alcohol is a good servant, but a bad master. As a servant it is one of the best solvents in the laboratory and the starting point in the manufacture of many such useful compounds as ether, chloroform and iodoform. Internal combustion motors can use it, with certain adjustments, and when our coal and oil deposits are exhausted the world will probably turn to cheap alcohol as a power fuel. It can be made from the starch and cellulose and sugars of plants, hence the sun's heat and power can be utilized in this way.

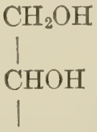
Alcoholic fermentation of sugars supplies us with all the ethyl alcohol used. Glucose is the only common fermentable sugar, so cane sugar, malt sugar, starch and cellulose must all be converted into glucose before they can yield alcohol. The reactions involved will be given later. During the Great War a Canadian company demonstrated the possibility of making alcohol from acetylene. This reaction is not used at present, but may be in the future.

Other Alcohols. — Glycerine is an alcohol, although we are inclined to forget that fact, since it is nonintoxicating. Its structure shows the presence of alcoholic hydroxyl groups, three of them in each molecule. Glycerine is a colorless, syrupy liquid of sweetish taste. Since it is hydroscopic (deliquescent) it keeps moist and is often put in mixtures because of this property. A great deal is used in plug tobacco and in some medicinal preparations, but most of it is converted into nitroglycerine. When fats are broken down in soap making, glycerine is a by-product. The same alcoholic hydroxyl is found in the sugars. A comparison of structural formulas of ethyl alcohol, glycerine and a typical sugar such as glucose is interesting. Ethyl alcohol may be represented as C_2H_5OH or $CH_3.CH_2OH$.



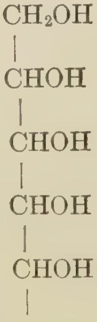
$$\begin{array}{c} CH_3 \\ | \\ CH_2OH \end{array}$$

Alcohol



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$$

Glycerine



$$\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHOH \\ | \\ CHO \end{array}$$

Glucose

Ethers. — The ether we know as an anesthetic is produced by the action of hot concentrated sulfuric acid in removing the elements of water from alcohol. In reality the reaction is more complicated, but the final result is dehydration.

In practice the vapors of methyl alcohol, mixed with air, are passed through a tube containing heated copper gauze as the catalyst:

$$2\,C_2H_5OH \rightarrow (C_2H_5)_2O + H_2O.$$

This diethyl ether, $(C_2H_5)_2O$, is a colorless liquid of very low boiling point, 35°, very inflammable, and only slightly soluble in water. It is a useful solvent for a great number of substances.

Dimethyl ether is $(CH_3)_2O$ and any ether could be represented as R_2O.

Isomerism. — It is a remarkable fact that common alcohol, C_2H_5OH, and dimethyl ether, $(CH_3)_2O$, have exactly the same percentage of carbon, hydrogen and oxygen and have the same vapor density. Therefore they have the same molecular weights and the formula for each must be C_2H_6O. But, as already stated, the atoms are linked together differently. Such compounds are called *isomers*. Their properties are quite different.

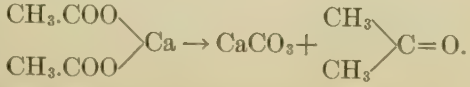
Aldehydes. — Wood alcohol can be oxidized moderately enough to fall short of becoming formic acid and thus formaldehyde may be secured. Other aldehydes are made in similar fashion. They are all reducing agents:

$$CH_3OH + O \rightarrow H.CHO + H_2O.$$

Formaldehyde is used as a 40 per cent solution called formalin. It is a much used germicide and antiseptic. A large amount is used to react with phenol (carbolic acid) in the preparation of "bakelite," a substitute for hard rubber. "Substitute" is a poor name here, for bakelite is superior to the hard rubber. By the use of formaldehyde, other similar plastics are made, such as "redmanol," etc. We see these useful materials as telephone receivers, handles for toilet articles, buttons, electric insulation material, fountain pens, pipe stems, and scores of familiar articles. Read the surprising chapter on Synthetic Plastics in Slosson's *Creative Chemistry*.

A comparison of the formulas of the various aldehydes in the series ($H.CHO$, $CH_3.CHO$, $C_2H_5.CHO$, etc.) shows that they all contain the characteristic group,— CHO. Thus the general formula for all aldehydes may be written R.CHO in which R represents any radical such as methyl (CH_3) or ethyl (C_2H_5).

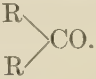
Acetone $(CH_3)_2CO$. — This colorless liquid is one of the products of the distillation of wood, but this does not produce enough for the demands of the industries, so more is made by dry distillation of calcium acetate:



$$\begin{matrix} CH_3.COO \\ CH_3.COO \end{matrix}\Big\rangle Ca \rightarrow CaCO_3 + \begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle C{=}O.$$

It is used as a safe solvent for compressed acetylene and in the manufacture of chloroform. It is a solvent for many substances such as fats and varnish materials and is of very great importance as a solvent in the manufacture of cordite and the various smokeless powders. During the early part of the Great War there was a wild scramble to get enough acetone. A huge "quick vinegar" plant was installed and the acetic acid converted into calcium acetate, which was then distilled for acetone. Every source was utilized.

Acetone is merely the simplest member of a series of *ketones* whose general formula is



$$\begin{matrix} R \\ R \end{matrix} \Big> CO.$$

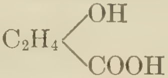
Acids. — There are different series of organic acids, but the "fatty-acid" series is the one of most common interest. The fats contain glycerine compounds of some of these acids, hence the name. All the members of this series are monobasic. Most of them are liquid, but such acids as palmitic and stearic are solids. Formic and acetic acids are the simplest members and the general formula may be written R.COOH.

Formic Acid, H.COOH. — Formic acid, H.COOH, is found in stinging nettles and red ants, adding zest to the sting or bite. It may be made by sufficient oxidation of methyl alcohol, but there is little demand for the acid.

Acetic Acid, $CH_3.COOH$. — The world has always known acetic acid at least in mixtures, for the fermentation of sugar in fruits has always produced alcohol, and this in contact with the proper organism (*mother of vinegar*) has always produced acetic acid. Sweet cider → hard cider → vinegar is a tradition, but thoroughly chemical just the same. Vinegar contains about 4 per cent of acetic acid and its preservative effects may be duplicated by a simple mixture of this acid and water. But we have a preference for the color and flavor connected with apple vinegar. Vinegars may be made from cider in a week or two if the *mother of vinegar*, which aids the oxygen of the air in uniting with the alcohol, be spread through a barrel of beechwood shavings (tasteless wood). Perforations in the barrel admit the necessary air and as the cider trickles through again and again, excellent contact is made. This was the process referred to in the discussion of acetone.

Acetic acid, when anhydrous, is a colorless liquid (*glacial acetic* *acid*) freezing to a crystalline solid at 18°. With water it forms a colorless solution. The odor is sharp, penetrating. *Sugar of lead* or lead acetate is one of its better known salts.

Other Acids. — Butyric acid, C_3H_7COOH, gives the characteristic odor to rancid butter. Oxalic acid, $(COOH)_2$, is found in some plants and is known to the public as a poison, as a hat cleaner and ink remover. Tartaric acid, $(CH_2OH)_2(COOH)_2$, is found in grapes, and its salt, acid potassium tartrate, is deposited in wine casks (or grape juice casks) as crude cream of tartar. It is used with sodium bicarbonate as a baking powder. Rochelle salt is sodium potassium tartrate. Citric acid, $C_3H_4(OH)(COOH)_3$, occurs in lemons, limes, grape fruit, etc. The last three acids are solids. Lactic acid,



$C_2H_4\left\langle\begin{matrix}OH\\COOH\end{matrix}\right.$, found in sour milk, is a liquid formed by the fermentation of milk sugar. Different organisms can bring this about. Some organisms can produce it from cane sugar. Its use as a food acid in soda fountain liquids and in other edible products is growing.

Esters. — Alcohols react with organic acids to form water and esters. These esters remind us somewhat of salts in their method of formation (but not in properties) and hence are often called ***ethereal salts.*** A comparison of the reactions producing inorganic salts and ethereal salts helps clear up the relations.

(1) $CH_3.COO\boxed{H}+K\boxed{OH}\rightarrow H_2O+CH_3.COOK$, potassium acetate.

(2) $CH_3.COO\boxed{H}+C_2H_5\boxed{OH}\leftrightarrows H_2O+CH_3.COOC_2H_5$, ethyl acetate.

Reaction (1) is neutralization of an acid by a base. A hydrogen ion from the acid unites with the hydroxyl ion from the base to form water. But reaction (2) is not neutralization, since the alcohol does not yield hydroxyl ions. All we can say is that the *hydroxyl group* of the alcohol unites with the *acidic hydrogen* of the acid to form water and that the hydrocarbon radical (C_2H_5) of the alcohol replaces the acid hydrogen of the acid, forming an ethereal salt, in this case ethyl acetate. In general esters may be represented by R.COOR′, where R and R′ are any hydrocarbon radicals. Inorganic acids also react with alcohols and the products are usually called esters also. Ethyl nitrate ($C_2H_5.NO_3$) is the ethyl ester of nitric acid. (How formed?) The so-called nitroglycerine is really glyceryl trinitrate, an ester of nitric acid and the alcohol glycerine.

EXERCISE 2. — How make methyl propionate? Propyl butyrate?

Many perfumes and flavors are esters. Amyl acetate smells like bananas to an intense degree. Ethyl butyrate reminds us of pineapples, although this ester can be made from the very offensive butyric acid. The student will enjoy the fascinating chapter on Perfumes and Flavors in Slosson's *Creative Chemistry*, and the similar chapter in Rogers' *Industrial Chemistry*.

EXERCISE 3. — Here is a chart comparison of typical organic compounds. Name each member.

HYDROCARBONS	HALOGEN DERIVATIVES	ALCOHOLS	ALDEHYDES	ACIDS	ETHYL ESTERS
CH_4	$CH_3.Cl$	CH_3OH	$H.CHO$	$H.COOH$	$H.COOC_2H_5$
C_2H_6	$C_2H_5.Cl$	C_2H_5OH	$CH_3.CHO$	$CH_3.COOH$	$CH_3.COOC_2H_5$
C_3H_8	$C_3H_7.Cl$	C_3H_7OH	$C_2H_5.CHO$	$C_2H_5.COOH$	$C_2H_5.COOC_2H_5$
etc.	etc.	etc.	etc.	etc.	etc.

Fats. — The esters derived from glycerine (as the alcohol) and the higher fatty acids such as palmitic and stearic (and oleic from a related series) are called fats. This means that fats are a particular kind of ester. We do not have to synthesize the fats — plants and animals have done that for us, but if desired it could be done:

$$C_3H_5(OH)_3 + 3\ CH.COOH \rightarrow (CH.COO)_3C_3H_5$$

glycerine + oleic acid → glyceryl oleate, a fat.

There are very few simple fats in animal and plant tissue. Olive oil is largely glyceryl oleate ("olein") but lard is a mixture of 40 per cent glyceryl palmitate (palmitin) and stearate (stearin) with 60 per cent olein. Beef suet contains the same fats but is harder because it contains only 25 per cent olein. Olive oil and cottonseed oil are liquids because they contain fully 75 per cent olein. Butter is a mixture of several fats. When it becomes rancid with age some of the esters are decomposed, yielding free acid, and the offensive odor of butyric acid makes itself known.

Oleomargarine is a butter substitute of good quality as a food. It is in great demand, for approximately 150,000,000 pounds of it are eaten annually in this country. To make it, beef fat from which much stearin has been removed by crystallization at 24° is stirred with some oil to soften it, and churned with milk to give it the butter flavor. On chilling, the "oleo" separates. It is colored by the consumers in order to avoid a heavy tax. The law does not permit it to be sold as butter.

Edible liquid fats are in great demand as salad oils and cooking oils. Olive oil is the most expensive, but recently enormous quantities of purified cottonseed oil, peanut oil and corn oil have found a ready market. The cheaper soya bean oil produced in Manchuria is used as a food in the Orient, but here it is chiefly used as a soap fat.

Soaps. — Esters are hydrolyzed by water, especially by hot water. The equilibrium reaction below indicates this:

$$CH_3.COOH + C_2H_5OH \leftrightarrows H_2O + CH_3.COOC_2H_5.$$

This hydrolysis takes place faster if a base is present. Of course a salt of the fatty acid must be formed.

$$\underset{\text{glyceryl oleate}}{C_3H_5(C_{18}H_{33}O_2)_3} + 3\ KOH \rightarrow \underset{\text{glycerine}}{C_3H_5(OH)_3} + \underset{\text{+potassium oleate, a soap}}{3\ C_{17}H_{33}.COOK}$$

This reaction is called saponification of the ester and the salt of the fatty acid is the soap. When a fat is saponified by hot water, glycerine and the free acid are the products. Soap-making on a commercial scale is simply a matter of boiling cheap mixed fats with caustic soda if the firm, "hard" soaps are desired, or with caustic potash if "soft" soaps are wanted. The soft soap of early pioneer days was made by using the lye (K_2CO_3) leached from wood ashes and such lard and tallow as accumulated about the house. Greater refinements are demanded now. Soap is "salted out" by common salt, partially dried and pressed into cakes. The remaining solution is distilled for its glycerine. By the Twitchell process fats are boiled with water and a complicated catalyst, yielding pure glycerine and the fatty acids. To make a soap from these acids is simply a matter of neutralization with a base.

Soaps of the unsaturated fatty acids such as oleic acid contain less water in the cakes than soaps of the saturated palmitic and stearic acids and in addition are more "soluble" in cold water. Hence for toilet use sodium oleate works better than sodium stearate or palmitate. In the boiling water of the laundry sodium stearate works well. The cleansing action of soap will be discussed under "Colloids."

Transparent soaps are made by adding glycerine or sugar or dissolving the soap in alcohol and allowing the solvent to evaporate. Scouring soaps contain mineral powders as abrasives. Floating soaps are light because of air bubbles beaten in while soft. Soap chips, much used for quick solution in laundries, are dried to contain little water. Only the soaps of the alkali metals are of value as cleansing agents.

EXERCISE 4. — When a soap is acidified, what are the products?

Carbohydrates. — A most important class of compounds including starch, the sugars and cellulose, contains carbon and just twice as many hydrogen atoms as oxygen atoms in each molecule. This means that the two latter elements are found in the proportion to form water, hence the name, carbohydrates. On heating, some of these give off water formed in the general decomposition but not held like water in hydrates. Plants take carbon dioxide from the air and water from the soil, building them into the cellulose of wood, cotton, linen, grasses, etc., or the starch of potatoes, arrow root, cassava, rice and the other roots and grains. Molecules of both starch and cellulose are probably large, represented by some multiple of $C_6H_{10}O_5$.

Cellulose. — Wood is, in general, made up of long fibers of cellulose $(C_6H_{10}O_5)_x$ cemented together by a gummy substance called lignin. In paper making this lignin is dissolved by digesting chips of the wood under pressure with a solution of calcium bisulfite, $Ca(HSO_3)_2$, or other reagents. The pulp of cellulose fibers is then shaken on a sieve through which the water drains and the fibers matted in a sort of "warp and woof" system. It is this interlacing that gives paper its strength. After passing through rolls to squeeze out the remaining water, a rosin size or glue size is spread over the surface to prevent undue spreading of ink. Usually the wet pulp is bleached and often dyed. Glazed papers that crack on creasing are loaded with clay, which gives body to the paper. The best writing paper may be made from linen rags. Cotton is nearly pure cellulose. The stringy part of vegetables is cellulose, but man makes little progress in digesting such fibers.

It has recently been proved at the United States Forest Products Laboratory that wood pulp heated under pressure with dilute acids to convert cellulose into glucose yields much of a partially hydrolyzed cellulose suitable for stock food. This is a useful contribution to human welfare, since our pastures are no longer capable of supporting enough cattle for our needs. To utilize waste wood as a stock food will make possible more beef and cheaper beef.

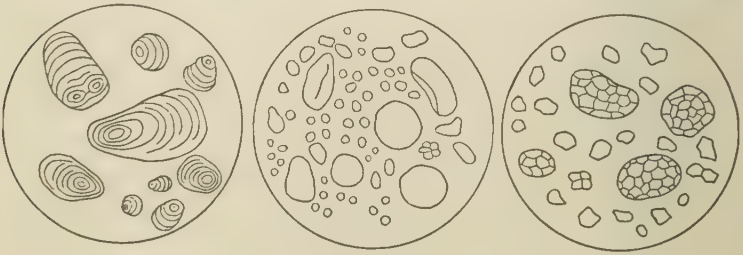
Cellulose is rather inactive chemically, yet it contains alcoholic hydroxyl groups and so should yield to the attack of acids. This occurs, but not readily. Prolonged acid treatment may convert much of it into glucose capable of fermentation into alcohol. There are a few plants operating successfully on this principle, making, not wood alcohol, but ethyl alcohol. Gun cotton, a high explosive, is an ester resulting from the attack of nitric acid on the cellulose of cotton. Wood cellulose can be used, but the cotton is preferred. With six nitrate groups per molecule the ester is an explosive, but under more gentle nitration only three or four nitrate groups may be introduced, forming "soluble gun cotton" or pyroxylin. This is dissolved in alcohol-ether to form common collodion, which, spun into threads, forms artificial silk. Dissolved in amyl acetate a useful lacquer is obtained, and this mixed with benzene, castor oil and lampblack provides a coating for patent leather. Pyroxylin mixed with camphor and a little solvent becomes celluloid, invaluable in countless ways. Our entire photographic film industry, including the motion picture division, owes its existence to cellulose esters. We were careful not to limit this statement to cellulose nitrate because cellulose acetate is a very similar ester of acetic acid and a sort of celluloid can be made from it. To tell the truth, it is better because noninflammable, but unfortunately it is more expensive and always will be. Some picture films are made of this "cellon" and they require no fireproof booth for public safety.

Cellulose is dissolved by zinc chloride and the pasty mass molded into so-called "fiber buckets" and the like. They are light, strong and can be given a waterproof surface.

Artificial Silk. — Enormous quantities of artificial silk are now being made from cellulose, as stated on page 247. Chemically it is very different from natural silk and it has even more luster than real silk. In the collodion process a solution of pyroxylin in alcohol-ether is forced through capillary tubes to make fine threads. The volatile solvent quickly evaporates and these threads may be woven together. However it is still nitrocellulose, too inflammable for safety, so the threads are denitrated in a suitable bath, thus reverting to the original cellulose of cotton. The glossy product differs from cotton only in its physical condition.

By the viscose process cellulose is treated with sodium hydroxide and carbon disulfide, forming a soluble compound called cellulose xanthate. This is spun and decomposed back into the original cellulose, but with the silken luster desired.

Starch. — Starch is stored in roots like potatoes, in grains, in chestnuts, and in the trunk of the sago palm (Fig. 87). It is a white substance of very high molecular weight $(C_6H_{10}O_5)_x$, insoluble in cold water, but swelling in hot water to a pasty translucent mass. When heated sufficiently it forms a yellowish, sweet substance called dextrin. The crust of bread (baked at a higher temperature than the moist interior) probably owes its sweetness to dextrin. Dextrin has been used as a mucilage on envelopes and postage stamps. Starch itself in the form of a paste is commonly used in hanging wall paper. It is a valuable food when cooked, but is far less digestible raw. Having alcoholic hydroxyl groups it can, of course, be nitrated. Nitro-starch is a very safe explosive and was used to the extent of thousands of tons in filling hand grenades. In the laundry, starch is indispensable. It is also one of the chief sources of ethyl alcohol. When treated with water and a trace of acid as a catalyst it is hydrolyzed into glucose.



1. Potato 2. Wheat 3. Rice

Starch Grains

FIG. 87

The Sugars. — There are two classes of soluble sugars, monosaccharides and disaccharides. The distinction is easy. Sugars of the formula, $C_{12}H_{22}O_{11}$, can be broken down into simple sugars, usually of the formula $C_6H_{12}O_6$. Such simple sugars cannot be resolved into still simpler sugars.

Complex sugars (Polysaccharides) $C_{12}H_{22}O_{11}$	Sucrose (cane sugar) Maltose (malt sugar) Lactose (milk sugar)
Simple sugars (Monosaccharides) $C_6H_{12}O_6$	Dextrose (glucose) or grape sugar Levulose (fructose) or fruit sugar Galactose Mannose Xylose, etc.

The sugars contain alcoholic hydroxyl radicals and, since there are several sugars of the formula $C_6H_{12}O_6$, there must be several different arrangements of the groups.

Sucrose, $C_{12}H_{22}O_{11}$. — Cane sugar, beet sugar and maple sugar are all the same when purified. However, none of us wants to purify maple sugar — we are all too fond of the flavor of its impurities. Americans eat more sugar than any other race, 90 pounds annually are consumed per person. It is a splendid food, yielding much energy quickly.

Sugar from cane is produced in Cuba, Hawaii, Java, Brazil and Louisiana — most of it in Cuba. The cane is crushed to extract the juice, which is then treated with lime to coagulate impurities that would otherwise ferment. The juice is next treated with carbon dioxide to precipitate the lime as calcium carbonate. The solution is boiled down in vacuum pans because if boiled at atmospheric pressure it would be decomposed. When the sugar crystallizes it is whirled free from molasses in centrifugals and shipped to refineries for further purification (see Carbon chapter).

Sucrose turns yellow-brown on heating, forming caramel, much used to color various food products.

The sugar beet is grown on great areas of France, Germany, Russia and in certain parts of the United States. Probably half the world's sugar is made from beets. There are certain special difficulties in extraction of the sugar, and the molasses is not palatable, but it is a profitable industry nevertheless. By careful breeding the sugar content of the beets has been increased to over 18 per cent.

Sucrose treated with acid as a catalyst reacts with water to form "invert sugar," a mixture of dextrose and levulose. Curiously enough this mixture, with some delicious impurities, makes up the main part of honey:

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \rightarrow \underset{\text{Dextrose}}{C_6H_{12}O_6} + \underset{\text{Levulose}}{C_6H_{12}O_6}$$

Glucose, $C_6H_{12}O_6$. — This is also called dextrose and even grape sugar since it occurs in grapes and raisins. It is less sweet than sucrose, but is a perfectly good food; in fact it is partly digested cane sugar. Both starch and sucrose, all the complex sugars in fact, are converted into glucose by the digestive fluids. Glucose is made commercially from starch which is heated with water and some acid as a catalyst:

$$(C_6H_{10}O_5)_x + x\ H_2O \rightarrow x\ C_6H_{12}O_6.$$

Hydrochloric acid is used in a 0.1 per cent solution. The trace of sodium chloride formed on neutralization with sodium hydroxide does no harm. Since corn starch is generally used as the raw material, the solution resulting is called "corn syrup." In addition to some water it contains 45 per cent of maltose, 20 per cent of glucose and 35 per cent of dextrin. The dextrin prevents crystallization of the glucose. Some of the table syrups are largely corn syrup, with some added cane sugar and even maple sugar for flavoring. Over 40,000,000 bushels of corn are converted into glucose annually in the United States. Glucose is used in candies, soda fountain syrups, baked goods and even as a filler for cheap soaps and leather. As an intermediate compound in the manufacture of alcohol (as well as whisky and beer) from the starch of cereals glucose has been of vast importance.

Glucose reduces Fehling's solution, precipitating yellow-red cuprous oxide, a reaction very useful in medical diagnosis.

Enzymes and Fermentation. — The yeast plant, a very lowly but useful organism made up of microscopic cells, secretes two chemicals known as invertase (or sucrase) and zymase. These are true catalysts. They are called enzymes because secreted by a living organism, thus differing from the inorganic catalysts. Sucrase splits sugar (in the presence of water) into glucose and fructose, both fermentable, although fructose is less so than the glucose. Zymase finishes the work begun by the sucrase and converts the simple sugars into alcohol and carbon dioxide:

$$C_6H_{12}O_6 \rightarrow 2\ CO_2 + 2\ C_2H_5OH.$$

It is an interesting fact that a germinating seed (barley, for example) develops enzymes as it sprouts. These catalysts, diastase and maltase, convert the insoluble starch of the seed into soluble glucose capable of being carried by the sap of the growing plant. The brewer borrows this clever device from the sprouting grain in order to make alcoholic drinks from starchy cereals. He allows barley to sprout, of course developing diastase and maltase in the process, then heats the sprouts to kill all life. The catalysts, mere chemicals, are uninjured. This "malt" is then mixed with the warm, moist, crushed grain and the starch is hydrolyzed to maltose, malt sugar, $C_{12}H_{22}O_{11}$. Yeast is then added and the malt sugar further hydrolyzed to form glucose. The zymase completes the change by fermenting this glucose into alcohol. By distillation a 45 or 50 per cent alcoholic solution well known as "whisky" is secured. Beer is simply the fermented liquor made from barley without distillation. Wine is fermented from grape juice by the wild yeast found on the skins of the grape. Even in as lawful a process as bread-making the yeast causes a fermentation with release of carbon dioxide and consequent "rising" of the dough.

Starch (by diastase) → maltose
Maltose (by maltase) → glucose
Glucose (by zymase) → alcohol

As a lecture table experiment, a solution of glucose or molasses may be mixed with fresh yeast and kept at about 30° for a day or so. Bubbles of carbon dioxide come off and, if led into a tube of clear lime water, precipitate white calcium carbonate. Finally the fermenting mixture may be distilled. The first few cc. of distillate contain alcohol sufficiently strong to burn. Alcohol boils at 78° and water at 100°, but in any mixture of the two the more volatile component does not come off completely at 78°. The first distillate collected at 78° and just above is richer in alcohol than those fractions collected at higher temperatures, but it is mixed with some water. As the temperature rises, the fractions become poorer in alcohol and richer in water up to 100°. Any fraction, say that collected from 80°–90° may be redistilled and it will begin to boil at 78° and rise to 100°. In practice a continuous process tower still is used. (See any industrial chemistry.)

There are other enzymes than those secreted by yeast or by sprouting grains. The animal body secretes enzymes which manage digestion of food. Pepsin is familiar to all of us. Molds also develop organic enzymes. As a rule they cause putrefaction. Bacteria contain enzymes. The study of molds, yeasts, and bacteria from the enzyme viewpoint is rapidly becoming a matter of commercial importance in the production of organic compounds. Such study is just now leading to the manufacture of large quantities of lactic acid as a food acid. During the Great War both

German and American chemists found organisms capable of making glycerine from sugar. Here is a limitless field for research.

FOOD

Plants feed on carbon dioxide, water, potassium salts, ammonium salts, nitrates and nitrites, but animals cannot assimilate any of these. Only complex compounds such as fats, protein and carbohydrates (with water) will nourish animals. Yet, with the exception of the sugars, these are all insoluble and cannot be carried in the blood and lymph. Luckily each animal carries its own laboratory in the form of stomach, intestines and glands. These by the process of digestion make the food soluble so it can pass through the body membranes.

Three great classes of foods are necessary to human health. The fats are found in meat, milk, nuts and the oils expressed from peanuts, cottonseed, corn, cocoanuts and soya beans. The carbohydrates are found as sugars in cane, beets, sweet fruits and as starch in the cereals, rice, potatoes, chestnuts and various tubers. Protein we get in lean meat, milk, cheese, beans, peas, eggs and the cereals. The protein molecule is very complex and very large, the molecular weight probably reaching several thousand. Protein always contains carbon, hydrogen, oxygen, nitrogen and usually sulfur.

Food is needed by the animal body to replace wornout tissues, provide for growth in the young, and supply heat to maintain the body temperature. Of course food is the source of all the bodily energy. When a muscle contracts tissue is oxidized and heat liberated. It has been definitely proved that the body is a very efficient sort of an engine. The same amount of energy in the ultimate form of heat is liberated when we eat and digest food enough to produce, say, 100 grams of carbon dioxide in the exhaled air as when enough coal is burned under a boiler to produce 100 grams of carbon dioxide. The average adult exhales 1100 grams of carbon dioxide, excretes 25 grams of urea and large quantities of hydrogen and oxygen in the form of water, daily. Protein is finally burned to urea.

In listing the food requirements it is important not to overlook the vitamines and the salts of iron, calcium, and other metals as well as compounds of phosphorus and iodine. The cellulose fiber of vegetable foods is not digested, but it is necessary to provide adequate bulk in the intestines.

Vitamines. — There are minute amounts of certain nitrogen compounds called vitamines absolutely essential to health. Their chemistry is not wholly clear to us yet, but apparently they are catalysts. We class them as *fat soluble A*, *water soluble B*, and *antiscorbutic C*. The fat soluble type is obtained largely in butter (or milk) and leafy vegetables. Evidently people eating oleomargarine should indulge in the free use of milk, spinach, and lettuce. It has just been found by Hawk that comb honey contains a moderate amount of fat soluble A. Water soluble B is plentiful in any varied diet. Babies, bottle fed, are given orange juice to supply this vitamine. Before the days of canned and properly dried fruits and vegetables, as well as refrigerators, sailors on long voyages suffered from scurvy, a deficiency disease. Their diet lacked vitamines. With the use of lemon juice and a more varied diet this disease has become historic. Yet in certain parts of China another deficiency disease called beri-beri has appeared. Very poor people living mainly on polished rice were afflicted. When investigators fed them the polishings from the rice grains, the sick recovered. The needed vitamines were on the surface of the rice grain and thus lost in the senseless polishing process.

Digestion. — There is very little digestion, aside from mechanical mastication, in the mouth. However, the enzyme ptyalin of the saliva does change a little starch to malt sugar. In the stomach the chief enzyme is pepsin of the gastric juice. Pepsin acts only in an acid medium, so the stomach is slightly acid with hydrochloric acid. Pepsin breaks down the highly complex protein molecules into proteoses and peptones which are further broken down by the trypsin of the small intestine into amino acids. These molecules are small enough to pass through the intestinal wall and are carried by the circulation to all parts of the body, there to be built up again into huge protein molecules. The whole effect of digestion is to facilitate transportation through the intestinal wall and to the various parts of the body.

Fats are emulsified by the bile and other alkaline juices of the intestine and split by lipase enzymes of the pancreatic glands into simple fatty acids and glycerine. These can pass through the intestinal wall and then are able to unite again, forming fat once more. Some fat is deposited in the tissues, but most of it is oxidized directly to carbon dioxide and water. Again the chief purpose of digestion is to get the fat through the intestinal wall. We are reminded of the recent method of getting large ships from Lake Erie through the Welland canal. The ships were cut in two, taken through the inadequate canal, and put together again in Lake Ontario.

Cane sugar (sucrose) must be split into glucose by an enzyme called sucrase. The glucose is easily absorbed and oxidized. Starch is partly digested by the ptyalin of the saliva and finished by the amylopsin of the pancreatic juice, which pours into the intestine. The maltose formed is then converted into glucose by the maltase. Diabetics are unable to oxidize all the glucose, so much of it appears in the urine and is there detected by its reducing action on Fehling's solution. This glucose does not cause the disease; it is merely the sign of it.

The Fuel Value of Food. — One gram of fat burned in the body yields 9 Cal. of heat (1 Cal. = 1000 cal.) and it yields but little more when burned in the calorimeter. If the fat were completely digested the two fuel values would be equal. One gram of protein yields 4 Cal. and one gram of carbohydrate yields only 4 Cal.

From the analysis of any given food one can readily calculate the energy value of a pound of that food (Fig. 88).

Exercise 5. — Consult the tables given in Sherman's *Food and Nutrition*, and local prices as secured from your stores. Then compute how many calories each of lean steak, of beans, of peas, of white bread, of potatoes, of milk, and of butter may be bought for one cent.

The Balanced Ration. — The average man not engaged in hard physical labor needs from 2500 to 3000 Cal. daily from his food. A football player or ditch digger may need 3000 to 4000 Cal. In order to build up muscular tissue, protein is required, but an excessive amount apparently does harm. Most authorities agree that about 100 g. of protein is enough per day for the business or professional man. This yields only 400 Cal. It would be possible to get the other 2100–2600 Cal. from butter — possible, but not advisable. The digestive system cannot take care of such quantities of fat, although the Esquimo nearly does it. It doesn't matter much just how the balance between fat and carbohydrates

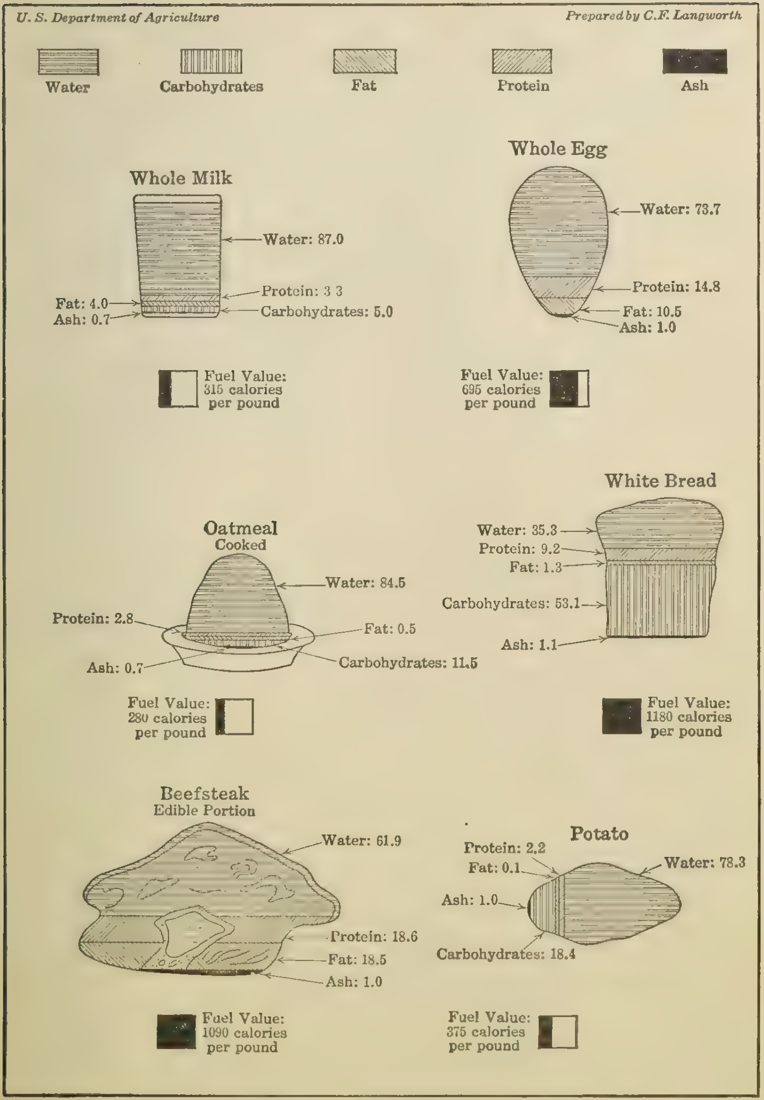

U. S. Department of Agriculture
Prepared by C.F. Langworth
Water
Carbohydrates
Fat
Protein
Ash
Whole Milk
Water: 87.0
Protein: 3.3
Fat: 4.0
Ash: 0.7
Carbohydrates: 5.0
Fuel Value: 315 calories per pound
Whole Egg
Water: 73.7
Protein: 14.8
Fat: 10.5
Ash: 1.0
Fuel Value: 695 calories per pound
Oatmeal
Cooked
Water: 84.5
Protein: 2.8
Fat: 0.5
Ash: 0.7
Carbohydrates: 11.5
Fuel Value: 280 calories per pound
White Bread
Water: 35.3
Protein: 9.2
Fat: 1.3
Carbohydrates: 53.1
Ash: 1.1
Fuel Value: 1180 calories per pound
Beefsteak
Edible Portion
Water: 61.9
Protein: 18.6
Fat: 18.5
Ash: 1.0
Fuel Value: 1090 calories per pound
Potato
Protein: 2.2
Fat: 0.1
Water: 78.3
Ash: 1.0
Carbohydrates: 18.4
Fuel Value: 375 calories per pound

FIG. 88

is struck, within reason. It seems well to eat about 100 g. of fat and 420 g. of carbohydrates. Modern research indicates that the complete digestion of fats is greatly aided by the carbohydrates.

With all this we use a fair amount of "horse sense." Spinach, lettuce, carrots and the fruits do not furnish much energy and might be neglected if we depend too much on energy values. However, vegetables and fruits are invaluable in furnishing needed salts and acids, as well as vitamines. Furthermore, the food must be palatable and digestible. A study of the food charts may lead to an undue enthusiasm for oatmeal (from the energy and financial standpoint), yet that same oatmeal diet may be irritating to the digestive tract. Dried beans, too, may be specialized in for similar reasons, but most digestions rebel in time. Food specialists are now urging the planting and more general use of the soya bean of Manchuria. As a food it is rich in fat and protein, contains some carbohydrate and both vitamines, fat soluble A and water soluble B.

FOOD CHART

Food	Protein, Per cent	Fat, Per cent	Carbohydrates, Per cent	Helping in Grams	Total Calories
Bread (white)	9.1	1.6	53.3	85	230.0
Butter	1.0	85.0		21	169.0
Beef (lean round)	19.0	13.0		128	250.0
Bacon (smoked)	10.5	66.0		28	188.6
Beans (fresh string)	17.0	1.5	5.0	113	48.7
Beans (baked canned)	9.6	5.5	3.3	92	182.0
Eggs (raw)	13.4	10.5		106	179.0
Fish (whitefish)	18.7	5.3		128	160.0
Fowls	18.0	11.5		99	110.5
Lamb chops (broiled)	21.7	29.9		57	210.0
Lettuce	1.2	0.3	2.9	28	7.0
Milk	3.3	4.0	5.0	170	123.6
Oatmeal	2.8	0.5	11.5	120	75.0
Potato (baked)	3.3	0.3	22.7	210	245.0
Orange	0.8	0.2	11.6	141	75.0
Peas (green)	4.3	3.3	6.7	85	103.0
Pie (apple)	6.5	6.9	32.0	127	283.0
Rice	2.8		24	113	125.0
Sugar			100.0	21	81.0

1 oz. =28.3 g.

NOTE: The fuel value of sugar and milk (or cream) must be added to the oatmeal serving.

Exercise 6. — From the above chart make out a menu for the three meals of the day, tabulating the weight in grams of each portion as near as can be estimated, the percentage of fat, protein and carbohydrate and the total fuel value of each portion. The total for the day must be 2500 Cal. and about 100 g. of protein must be included. The calculations must be based upon the analyses given in the table. More extensive tables are found in books by Sherman and Weed given in the following list of references:

Suggested Reading

"Industrial Alcohols," *Jour. Ind. Eng. Chem. 12*, 370, 1920.

Chemistry of Food and Nutrition, Revised Edition (Sherman). The Macmillan Co.

Food Products (Sherman). The Macmillan Co.

Pure Foods (Olsen). Ginn & Co.

Elementary Household Chemistry (Snell). The Macmillan Co.

The Newer Knowledge of Nutrition (McCollum). The Macmillan Co.

Chemistry in the Home (Weed), pages 250–282. American Book Co.

Principles of Human Nutrition (Jordan). The Macmillan Co.

Everyman's Chemistry (Hendrick). Harpers.

Industrial Chemistry (Rogers), for the Chapter on Baking. D. Van Nostrand Co.

The book that every student should own is Slosson's *Creative Chemistry*, The Century Co. All of it is fascinating, but at this time special attention should be given to the chapters on: Coal-tar Colors, Synthetic Perfumes, Cellulose, Synthetic Plastics, The Rival Sugars, What Comes from Corn, Solidified Sunshine.

CHAPTER XXIV

SILICON AND BORON

SILICON

Silicon resembles carbon in its valence of four and in the weakly acid properties of its hydroxide. It also forms a series of compounds remarkably like the compounds of carbon. For example, SiH_4 is comparable to CH_4; $SiCl_4$ to CCl_4; and $SiHCl_3$ (silicochloroform) to $CHCl_3$ (chloroform). There are many more such compounds of silicon, but they differ from carbon compounds in that silicon atoms will not link up with each other in large molecules as do carbon atoms. The limit in stability of such chain compounds is represented by Si_6H_{14}.

Occurrence. — Silicon does not occur free but it is the commonest element after oxygen. Over one fourth the earth's crust is combined silicon. Its oxide (SiO_2) is found everywhere as quartz or in sand and sandstone. Clay and all common rocks except limestone and dolomite are silicates. Silicon is the central element of the mineral world much as carbon is in the plant and animal realm.

Preparation. — The preparation of the element by reduction of the oxide is not easy. However, magnesium and aluminum when ignited, have tremendous reducing power and are employed with success in this case. They are used in the powdered form:

$$2\ Mg + SiO_2 \rightarrow 2\ MgO + Si \text{ (amorphous)},$$
$$4\ Al + 3\ SiO_2 \rightarrow 2\ Al_2O_3 + 3\ Si \text{ (crystalline)}.$$

The silicon is obtained crystallized from aluminum because it is dissolved by the excess molten aluminum and has opportunity to crystallize on cooling. The amorphous form may be crystallized from molten zinc. Dilute acid dissolves either aluminum or zinc, leaving the shining needles of silicon.

Carbon reduces the oxide at the high temperature of the electric furnace and large quantities are now made that way. The process resembles the manufacture of carborundum except that less coke is used. When a mixture of iron oxide and silicon dioxide is reduced with carbon, ferrosilicon is produced. It is much used in steel making to remove air bubbles. The hot silicon unites with oxygen. An iron alloy containing 14 per cent silicon, known as Duriron, is used for condensers in nitric acid plants because of its remarkable resistance to the attack of acid. This alloy is very hard and brittle.

Properties. — Amorphous silicon is a brown powder, while the crystalline form is obtained in hard, black, hexagonal needles. It melts at 1450° and cools to a brittle, silvery mass. The element is readily attacked by the halogens, forming gases. With chlorine it reacts at 430° and with oxygen at 400°. At high temperatures it forms silicides like CSi. As stated in the Hydrogen chapter silicon displaces hydrogen from hot solutions of sodium hydroxide. This is a convenient military method of making hydrogen for balloons:

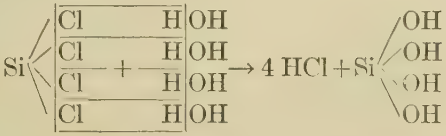
$$4\ NaOH + Si \rightarrow Na_4SiO_4 + 2\ H_2.$$

Exercise 1. — Is pure silicon used in this process?

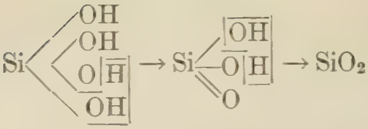
Silicon Tetrachloride, $SiCl_4$. — This colorless liquid boiling at 59° is made by direct union of silicon and chlorine at 430°:

$$Si + 2\ Cl_2 \rightarrow SiCl_4.$$

It used to be prepared by the combined attack of hot carbon and chlorine on silicon dioxide, the carbon pulling at the oxygen and the chlorine at the silicon. The liquid fumes badly in moist air and so was used to some extent in producing smoke screens for military purposes. Water hydrolyzes it completely, forming orthosilicic acid. Compare this with the hydrolysis of the chlorides of phosphorus:



The Silicic Acids. — Orthosilicic acid is prepared by hydrolysis of the chloride or decomposition of silicates with acids. It is such an extremely weak acid that its ammonium salt has never been isolated, due to its complete hydrolysis. By progressive dehydration orthosilicic acid is finally converted into its anhydride, silica (SiO_2). The loss of water is facilitated by heating.



Ortho-silicic acid — Meta-silicic acid — Silica, SiO_2

The loss of water is so steady that not a single pure silicic acid has yet been prepared. For this reason they may be regarded as $SiO_2.x\ H_2O$. Victor Lenher applied a pressure of 600,000 pounds per sq. in. to ordinary silicic acids and reduced the amount of water to correspond to $\frac{H_2O}{2}.SiO_2$. Probably greater pressures would cause a greater loss of water. However, salts of the different acids are found as minerals. Water may be lost in such a way as to join two or more molecules forming disilicic acids (containing two silicon atoms) or trisilicic acids (containing three silicon atoms).

$$2\ H_4SiO_4 \rightarrow H_2O + H_6Si_2O_7$$
$$2\ H_4SiO_4 \rightarrow 2\ H_2O + H_4Si_2O_6$$
$$2\ H_4SiO_4 \rightarrow 3\ H_2O + H_2Si_2O_5$$
$$3\ H_4SiO_4 \rightarrow 5\ H_2O + H_2Si_3O_7$$

A convenient laboratory method of preparing silicic acid is to acidify a soluble silicate such as "water glass" (Na_2SiO_3):

$$Na_2SiO_3 + 2\ HCl \rightarrow 2\ NaCl + H_2SiO_3.$$

A water glass solution of 1.16 sp. gr. may be added to approximately 8 per cent hydrochloric acid. With proper precautions the entire mass turns into solid jelly, more water being held by the silica than is called for by the formula. This jelly may be washed, and then dried in the oven to a fine powder (SiO_2). In the following chapter there is more about silicic acid.

The so-called "silica gel" now on the market for gas adsorption purposes is merely extremely fine silica powder prepared by dehydrating the precipitated acid in a vacuum at about 300°. It holds a few per cent of water and readily adsorbs a great deal more, making a good drying agent. Many industrial gases are adsorbed and given off again on heating, so its use in gas recovery will grow.

Silica, SiO_2. — Quartz or silica is one of the common minerals. It crystallizes in six-sided prisms as rock crystal. One crystal in California weighs over a ton. These crystals are often colored beautifully by impurities. Smoky quartz, rose quartz, and amethyst are well known.

Amorphous silica is found as agate, jasper and onyx, also colored by impurities. Opal and flint are slightly hydrated forms, as is the solid material of some sponges. Infusorial earth (tripoli), much used as a polishing powder, for making dynamite, and in packing, is composed of the siliceous remains of minute organisms. The stems of straw, bamboo and horsetail contain silica.

Sand is partly disintegrated quartz and when the grains are cemented together with silica or lime under nature's pressure, sandstone results. Iron oxide impurities often give it color. In smoky cities sandstone with a lime cement is disintegrated by the acid nature of the smoke.

Above 900° quartz is slowly converted into rhombic crystals with a density of 2.2, while below that temperature the hexagonal crystals with a density of 2.0 are stable. Quartz melts at 1600°–1750°, but it is difficult to observe any sharp melting point. It softens gradually, due to its great viscosity even when fluid.

As the anhydride of an acid it reacts with bases but not with acids (except hydrofluoric acid). With fused sodium carbonate it displaces carbon dioxide, as would any ordinary acid. The volatility of one of the products, carbon dioxide, prevents reversal of the reaction:

$$Na_2CO_3+SiO_2 \rightarrow Na_2SiO_3+CO_2.$$

Silica reacts with hydrofluoric acid with formation of the gas silicon tetrafluoride:

$$SiO_2+2\,H_2F_2 \rightarrow 2\,H_2O+SiF_4 \uparrow$$

Water Glass. — Water glass may be made in two ways. Sand is boiled (under pressure) with a strong solution of sodium hydroxide, or sand is treated with fused sodium carbonate. In either case sodium metasilicate is formed:

$$SiO_2+2\,NaOH \rightarrow Na_2SiO_3+H_2O,$$
$$SiO_2+Na_2CO_3 \rightarrow Na_2SiO_3+CO_2.$$

Water glass is sold in great quantities in the form of a concentrated solution, a thick syrup of about 1.38 specific gravity. When allowed to dry it forms a brittle, glassy solid. As a salt of a weak acid and a strong base (see Hydrolysis) its aqueous solution has a strongly basic reaction:

$$Na_2SiO_3 + 2\ H_2O \leftrightarrows 2\ NaOH + H_2SiO_3.$$

Of course free silicic acid must be present yet we know it is insoluble. In a freshly diluted solution none can be seen. The explanation is found in the next chapter — the acid particles are too small to be seen and are spoken of as in colloidal suspension. On long standing these small particles of silicic acid aggregate and settle out as a visible precipitate.

Water glass has a variety of uses. It is the cheapest glue known. The heavy cardboard shipping boxes of to-day are built up from paper sheets glued together. Artificial stone is prepared from small lumps of stone and sand, with a water glass binder. Wood, cloth and paper are fireproofed with water glass. It is a filler and binder in cheap soaps. One part of the common commercial syrup mixed with ten to fifteen parts of water, boiled to remove carbon dioxide, is an excellent egg preservative. In applying water glass to new uses, it must be remembered that it dries to a very hard, brittle mass.

The composition is varied by the manufacturers to suit special needs. The material approximating the formula Na_2SiO_3 is very alkaline and readily soluble. Usually a higher proportion of silica is used, making the product less alkaline, somewhat less readily soluble, but cheaper, since sand is cheaper than soda. $Na_2SiO_3.3\ SiO_2$ represents a very common product.

EXERCISE 2. — How many grams of water glass can be made from 150 g. of pure sand? If fused with soda, how many liters of carbon dioxide would be released?

Silicate Minerals. — Although it is difficult if not impossible to isolate definite silicic acids, salts of several different ones are found as minerals.

Orthosilicates (from H_4SiO_4)	Mica, $KH_2Al_3(SiO_4)_3$ Kaolin, $H_2Al_2(SiO_4)_2.H_2O$ Garnet, $Ca_3Al_2(SiO_4)_3$
Metasilicates (from H_2SiO_3)	Asbestos, $CaMg_3(SiO_3)_4$ Soapstone or talc, $Mg_3H_2(SiO_3)_4$ Beryl, $Gl_3Al_2(SiO_3)_6$
Disilicates (from $H_6Si_2O_7$)	Serpentine, $Mg_3Si_2O_7.2\ H_2O$
Trisilicates (from $H_4Si_3O_8$)	Orthoclase; $KAlSi_3O_8$

In decomposing these silicates for analysis they are powdered and fused with sodium carbonate:

$$CaSiO_3 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SiO_3.$$

The silicates dissolve in melted soda, while carbonates do not, so the reaction is not reversible. On addition of hydrochloric acid everything dissolves. Evaporation of the residue dehydrates the silicic acid liberated from sodium silicate. This is finally weighed as pure silica. The soluble chloride of calcium (or other metal) is removed and determined by the usual methods.

EXERCISE 3. — Write the equations representing the action of hydrochloric acid on the fusion product just discussed.

Glass. — Glass is a mixture of silicates, usually of sodium and calcium, although many variations are possible. Common glass might be considered as $Na_2SiO_3.CaSiO_3$, but in practice more silica is added. (Compare with water glass.) Window glass is usually $Na_2O.CaO.6\,SiO_2$. This does not mean that Na_2O is actually present as such. The formula is merely a convenient representation of an analysis.

Glass is made by melting sand, lime and soda in a gas-heated furnace. If iron be present as an impurity, the glass is green. This is the color of ferrous silicate. Since ferric silicate has a very weak yellow color it is an advantage to oxidize the green ferrous salt with manganese dioxide. Too much manganese introduces the amethyst of manganese silicate. Soft, or low melting, glass is of the lime-soda type. Hard glass, of higher melting point, is prepared by substituting potassium carbonate for the sodium carbonate.

Window glass is blown from a ball into a cylinder, cut open while hot, and allowed to flatten in the annealing oven. Bottles are made by blowing the glass in a mold. Plate glass is cast on a wide iron table, rolled flat and, when cold, ground to remove unevenness and polished with rouge. Flint glass is used for optical work and in making cut glass because of its high index of refraction. Lead is here substituted for calcium. Flint glass is "cut" on a grinding wheel into ornamental designs. When the pattern is deep the glass is molded, but the surfaces need polishing to make them smooth facets for the diamond-like sparkle desired. Dilute hydrofluoric acid is now used in polishing cut glass.

Colored glasses are made by addition of cobalt compounds for blue; gold, cuprous oxide or selenium for red; manganese dioxide for amethyst; chromium oxide for green; and uranium oxide for yellow. Resistance glass of the Jena or pyrex type contains some boron trioxide in place of part of the silica. It resists the attack of chemical reagents very well and is essential to the laboratory. During the war the Allies suffered for want of chemical glass formerly made in Austria and Germany. Necessity proved to be the mother of invention, for we now make chemical glass superior to the best produced abroad.

Glass is often spoken of as a "supercooled liquid," by which we mean that on cooling from the viscous liquid condition, it has not crystallized as a pure compound should. It is plastic and amorphous. If it be considered as a solution of one silicate in another its behavior is understandable. On holding near, but below, its melting point for a long time, one of the components does crystallize, forming "milk glass."

Enamels are glasses varied somewhat in composition. They are made white by suspended tin oxide or calcium phosphate or fluorspar.

Quartz glass is nothing but pure silica. Its melting point is so high and the liquid obtained so viscous that the skilled labor involved in manufacture makes it expensive. Air bubbles are difficult to remove from the melt. Since its coefficient of expansion is low, this glass may be heated red-hot and cooled instantly in cold water without cracking. Vessels of it withstand acids (but not bases) and so have special uses. Transparent quartz is useful in optics and in ultraviolet lamps, because it is permeable to ultraviolet light, unlike ordinary glass.

EXERCISE 4. — How could you make a blue enamel?

BORON

Boron, with a valence of three, belongs with the aluminum family and not with tetravalent carbon and silicon. It is a more pronounced acid former than aluminum and in chemical properties is much nearer silicon.

Occurrence. — The element is not found free but as boric acid, borax, boracite, and colemanite. Boric acid, $B(OH)_3$, occurs in certain springs in Italy. On cooling, greasy, white crystals are deposited. Borax, $Na_2B_4O_7$, is found in Death Valley, California. Boracite, a complex magnesium salt, is found in the Stassfurt mines. Colemanite, $Ca_2B_6O_{11}.5\,H_2O$ is plentiful in California.

Preparation. — The oxide is difficult to reduce to the element, but hot magnesium powder will do it:

$$B_2O_3 + 3\ Mg \rightarrow 2\ B + 3\ MgO.$$

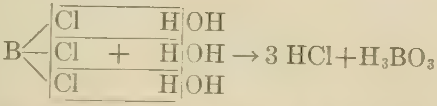
The product may be amorphous and black, but if reduced by excess of aluminum, boron, or rather AlB_{12}, crystallizes from the molten aluminum. (How get rid of the aluminum?) A pure form of the element is obtained by reduction of the chloride with hot hydrogen:

$$2\ BCl_3 + 3\ H_2 \rightarrow 2\ B + 6\ HCl.$$

Properties. — Boron is gray and has a melting point above 2000°. It is nearly as hard as diamond. Its electrical resistance decreases enormously with rise in temperature. Boron unites with the same elements as silicon but is more active. Fused potassium hydroxide attacks it:

$$6\ KOH + 2\ B \rightarrow 3\ H_2 + 2\ K_3BO_3.$$

Boric Acid, H_3BO_3. — The combined attack of hot carbon and chlorine on the trioxide yields boron trichloride. This liquid (boiling at 18°) fumes in moist air and is completely hydrolyzed, forming boric acid.



$$B\begin{matrix} Cl & & H \\ Cl & + & H \\ Cl & & H \end{matrix}\begin{matrix} OH \\ OH \\ OH \end{matrix} \rightarrow 3\ HCl + H_3BO_3$$

Boric acid, as was mentioned, occurs in some hot springs. It is also prepared by acidifying borax solutions:

$$Na_2B_4O_7 + 5\ H_2O + H_2SO_4 \rightarrow Na_2SO_4 + 4\ B(OH)_3.$$

It is very faintly acid and so its use as a mildly antiseptic eyewash is not complicated by hydrogen ions. There is some question about the existence of its salts. Purification of this acid is easy because it is volatile with steam. Identification is also easy since it imparts a green color to a gas flame. On heating to 100° it changes by partial dehydration to the metaboric acid, at 140° to tetraboric acid, and at higher temperatures to the anhydride. Boron trioxide is a hygroscopic glassy solid.

$$\underset{100^\circ}{H_3BO_3 \rightarrow} \underset{140^\circ}{HBO_2 \rightarrow} H_2B_4O_7 \rightarrow B_2O_3$$

Borax. — Most of the borax in the United States is made from colemanite.

$$2\ Ca_2B_6O_{11}+4\ Na_2CO_3+H_2O \rightarrow 4\ CaCO_3+2\ NaOH+3\ Na_2B_4O_7$$

Borax crystallizes from solution at 56° with 5 H_2O of crystallization and at 27° with 10 H_2O. It can be made by neutralizing boric acid. We are reminded here that when borax is acidified, boric acid is obtained:

$$4\ H_3BO_3+2\ NaOH \rightarrow 7\ H_2O+Na_2B_4O_7.$$

Since borax is a salt of a strong base and a weak acid, its solutions are basic by hydrolysis. Of course, this hydrolysis increases with dilution, as may be shown by addition of silver nitrate to concentrated and dilute solutions. White silver borate is precipitated from the concentrated borax solution, but brown silver oxide from the dilute solution. In the latter case silver hydroxide was first formed, which with loss of water became the oxide. Since borax solutions are strongly basic it is useful in softening water and in cleansing. As a flux in soldering it has another use. The formula might well be written as 2 $NaBO_2.B_2O_3$, which shows that borax is really sodium metaborate with the acid anhydride. When melted between hot metal plates, as in welding or soldering, this acid anhydride reacts with metallic oxides (rust) to form easily fusible slags which are squeezed out, leaving clean metal surfaces for good contact.

Borax beads are used in analysis in much the same way. Some powdered borax is picked up on a loop of platinum wire and heated in the flame to expel water of crystallization. A clear, glassy bead results. This is touched to a minute fragment of the substance to be tested and heated again. In the case of a cobalt compound, a blue bead results. Some cobalt oxide is formed on heating and this reacts with the acid anhydride (B_2O_3) part of borax to form a cobalt borate. The blue glass really is a double salt, sodium cobalt metaborate, 2 $NaBO_2.Co(BO_2)_2$. Other compounds give different colored beads. These beads resemble the colored silicate glasses. In fact, polysilicates would serve as well as borax beads in analysis if they melted at convenient temperatures. Some enamels are of this type.

Borax solutions turn turmeric paper brown. Acidified borax colors a gas flame both yellow (due to the sodium) and green (due to the liberated boric acid).

Exercise 5. — Hot boron unites with nitrogen to form a white solid. What must be the formula and name? What similar compounds have been studied?

Exercise 6. — In the electric furnace, boron unites with carbon to form boron carbide, one of the hardest substances known. What similar reaction and product have you studied?

CHAPTER XXV

COLLOID CHEMISTRY

Strictly speaking, there are no such things as ***colloids,*** for most, if not all, substances can be prepared in the "colloidal state." However the term *colloid* is too convenient to drop.

"Colloid chemistry," writes Bancroft, "is the chemistry of grains, drops, bubbles, filaments and films." This is a useful conception. By grains we mean small solid particles. Drops are small liquid particles, and bubbles small gas particles. In filaments, all dimensions but one are very small, while in films only one dimension is small. These particles must be surrounded by, or dispersed in, some other substance.

Grains	dispersed in another solid	gold in ruby glass sodium in blue rock salt elements or compounds in some alloys
	dispersed in a liquid	colloidal gold in water colloidal selenium in water
	dispersed in a gas	dust visible smoke
Drops	dispersed in a solid	water in butter
	dispersed in a liquid	oil-in-water emulsions (milk)
	dispersed in a gas	mist fog
Bubbles	dispersed in a solid	air in meerschaum air in pumice stone
	dispersed in a liquid	foam
	dispersed in a gas	impossible because gases mix intimately as in liquid solutions
Filaments	any solid fibrous material may contain filaments of minute diameter	
Films	films may be liquid or solid, but they must be very thin; soap bubble films have one colloidal dimension	

But after all we are colloidally interested in grains, drops, and bubbles only when they are sufficiently small, of diameters ranging from about 100 $\mu\mu$ to 1 $\mu\mu$. (A millimicron, 1 $\mu\mu$, is one millionth of a millimeter.) The smallest particle visible with the aid of the best microscope is about 100 $\mu\mu$ in diameter, while the largest molecules approach a diameter of 1 $\mu\mu$. The colloidal realm ranges, then, from the lower limit of microscopic visibility to the upper limit of molecular dimensions. Colloidal chemistry is a mere matter of size of particle. Each colloidal particle is an aggregate of hundreds or thousands of molecules.

New properties of matter appear when a given substance is colloidally dispersed. The effect of gravity is counteracted, while surface tension, electric charge, and other forms of energy increase greatly. Gold, yellow in the mass, may be coarsely dispersed in water to form what is apparently a green solution. With still finer dispersion it is blue or purple, and when just short of molecular dispersion is cherry red. The brightest red particles of gold are about 6 $\mu\mu$ in diameter.

Add a saturated solution of mercuric chloride to a brown suspension of colloidal silver. The color disappears, and a white precipitate of mercurous chloride and silver chloride is found. ($HgCl_2 + Ag \rightarrow AgCl + HgCl$.) In this case the reducing action of silver has been greatly magnified, due to its relatively great surface.

Why Colloidal Particles Remain in Suspension. — Gold is much heavier than water, yet many red-gold suspensions in water have been kept for years without settling. If the water were frozen to solid ice we might understand this nonsettling as we do in the case of ruby glass. There are at least three good reasons for the stability of ordinary colloid suspensions. These are the Brownian movement, the presence of electric charges on particles, and of protecting films around them.

1. *Brownian Movement.* — If a heavy steel ball were suspended by fine wire, a light tap with a pencil would certainly move the ball, almost imperceptibly. The same light tap of the pencil must move a suspended baseball quite appreciably, and must produce exaggerated motion in a light pith ball. In each case the kinetic energy is the same, so the greater the mass of the ball, the less the distance moved.

In order to magnify the distance moved by a bombarded particle it is only necessary to diminish the size of the particle sufficiently. Consider a colloidal gold suspension. The water molecules, always in constant motion when above absolute zero, bombard the suspended particles of gold from all sides. The gold particles are moved some distance, of course, but when such particles are large enough to be visible, this motion is too slight to be of much help and the gold settles rapidly. But gold aggregates under 100 $\mu\mu$ in diameter are projected appreciable distances by the water molecules. This vigorous stirring effect is perpetual. Under the lens of the ultramicroscope this Brownian movement is startling. The gold particles dart with zigzag motion in all directions (Fig. 89). At this point the observing student remembers that colloidal gold particles are not visible under the microscope. How then is this motion apparent? The suspension is examined in a dark field while a strong beam of light entering at right angles to the line of vision makes the gold particles visible as mere points of light without apparent diameter. This Brownian movement furnishes convincing proof of the reality of molecules, the molecules that do the bombarding.

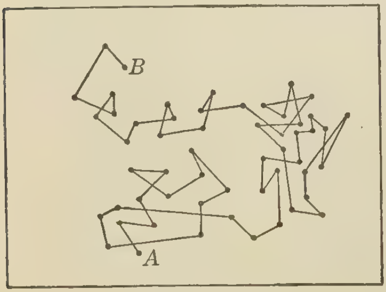


Fig. 89

The suspended colloid particles must have kinetic energy of their own just as truly as have the molecules, but being heavier their actual motion is less. No doubt some molecules have much greater kinetic energy than the average and hence the impacts against one side of a very small colloidal particle are not always balanced by impacts of equal force on other sides. The result is that colloid particles actually travel in a zigzag path.

2. *Electric Charge.* — Most colloid particles move slowly in an electrolytic cell as if attracted by the charged poles and are coagulated into coarse aggregates on contact with the attracting poles. This means that the particles are electrically charged bodies. In some suspensions, such as arsenic sulfide, all the particles are attracted to the anode, hence are negatively charged. Ferric hydroxide particles are all positive. Particles bearing like charges,

free to move, must repel each other, thus tending to remain scattered or suspended throughout the liquid.

3. *Protecting Films.* — A film of gelatin or of various gummy substances can surround each suspended particle so that they have difficulty in touching. Under such conditions coalescence into aggregates too large for help from the Brownian movement is difficult. Any influence tending to keep the aggregates small aids stability.

Methods of Preparation. — There are several methods of subdividing the common insoluble substances so that the substances become colloidally suspended. Some methods are purely mechanical and others are chemical. It must be remembered that although these suspensions may look like true solutions to the eye, they are not true solutions. The effect of suspended material on osmotic pressure, freezing-point lowering and boiling-point rise is trifling, as might be expected from the smaller number of particles per gram of suspended matter as compared with number of particles (molecules) from a gram of matter in true solution. Each colloid aggregate is hundreds or thousands of times as large as a molecule.

1. *Grinding.* — The simplest method in principle but of little value in practice, is fine grinding. This applies to some extent when the solid to be dispersed is brittle. In the early days of tungsten lamp development, Kuzel made colloidal tungsten by long grinding in a ball mill. Richardson has prepared catalytic nickel for hydrogenation of liquid fats and Lenher has made colloidal silica by the same method.

2. *Peptization by Liquids.* — By peptization we mean disintegration into colloidal particles through the action of some added chemical. Water has long been used as a peptizing agent in *dissolving* glue, gelatin, agar, and such substances. In reality, the glue or gelatin was not dissolved in the true sense of molecular dispersion, but only colloidally dispersed. Hot water has a more rapid peptizing action than cold. Acetone is said to dissolve pyroxylin but it only peptizes the solid.

3. *Peptization with Ions.* — Colloid particles have an ability to hold to their surfaces, to adsorb, other substances, even ions. A given surface may have a preference for certain ions and thus in one case acquire a positive charge by holding a positive ion, charge

and all, while another kind of colloid may choose to acquire a negative ion and charge. This reminds us of one of the reasons for stability — like charges on the particles. It is thus evident that a colloid may be stabilized, kept in suspension, by adsorption of ions.

To demonstrate this, arrange a series of tubes containing definite quantities of silver nitrate, for example, 15 cc. of 0.05 N solution. From a burette add to the middle tube exactly 15 cc. of 0.05 N potassium bromide, an equivalent amount. To other tubes add a slight excess of the potassium bromide, perhaps 15.1 cc., 15.2 cc., 15.3 cc., 15.5 cc., 16 cc. In the opposite direction add a little less than an equivalent amount of potassium bromide, perhaps 14.9 cc., 14.8 cc., 14.7 cc., 14.5 cc., 14 cc., etc. In all cases stir or shake while adding the second solution. If the work be accurately done, the mixture of equivalent amounts of silver nitrate and potassium bromide produces a quick-settling precipitate of silver bromide. Those containing a slight excess of silver nitrate do not yield precipitates but milky suspensions. If these suspensions are placed in an electrolytic cell under proper conditions the suspended particles move to the cathode, hence are positively charged. They must have gained this positive charge by adsorbing the excess silver ions. In the opposite direction the silver bromide adsorbs bromide ions from the excess of potassium bromide, becoming negative and yielding a suspension. The question may be asked, "Why does not the silver bromide adsorb nitrate ions as well as silver ions?" Because it has a preference for particular ions.

As a corollary to this principle, there may be added the statement that precipitates are sometimes peptized by washing out the precipitating ions. This really means that the proper ionic concentration for suspension is secured. In analysis precipitates are often inclined to run through the filter on washing. Wash waters containing ammonium salts are then used to coagulate the suspension. Fortunately such salts may later be removed by ignition.

4. *Formation in Low Ion Concentration.* — A familiar reaction is that between hydrogen sulfide and arsenic trichloride:

$$(1)\ 2\ AsCl_3 + 3\ H_2S \rightarrow 6\ HCl + As_2S_3.$$

The yellow sulfide settles out quickly. Yet if some arsenious oxide be boiled in water and the solution filtered, any addition of hydrogen sulfide fails to yield a precipitate. A lemon-yellow suspension is obtained:

$$(2)\ As_2O_3 + 3\ H_2S \rightarrow 3\ H_2O + As_2S_3.$$

The essential difference between (1) and (2) is that in (1) the by-product is an acid which ionizes, while in (2) the by-product is only water. Addition of a little hydrochloric acid or even some salt to the yellow colloid suspension coagulates the sulfide, with consequent quick settling. The suspended particles are negatively charged, and it is obvious that this charge could be neutralized by positive ions such as hydrogen, sodium and others. Loss of charge means less ability to remain suspended.

To secure a suspension of any insoluble salt while forming, there is required an absence of oppositely charged ions or at least a very low concentration of such ions.

Copper sulfide is negatively charged in suspension, but such suspensions cannot be secured by reaction of hydrogen sulfide with a solution of a copper salt. The positive copper ions, necessary to the reaction though they are, immediately discharge and thus coagulate the copper sulfide as fast as it is produced. If we could only tie up the offending copper ions in some reservoir that automatically releases a few at a time as needed, the production of colloidal cupric sulfide should be possible. This can be done by adding Rochelle salts or any tartrate to tie up the copper in a complex molecule yielding but few cupric ions in equilibrium. The manipulation is not simple, for this colloid is sensitive.

5. ***Reduction.*** — Salts of gold, silver, mercury, platinum and palladium are easily reduced to the free metal. Under favorable conditions beautiful suspensions form. Very dilute gold chloride solutions made neutral by a trace of potassium carbonate are reduced almost too easily. Casual impurities such as those introduced by contact with the finger may produce red or blue gold.

Mix 2 cc. of 1 per cent gold chloride solution with 98 cc. of water. Dissolve 0.5 g. tannin in 100 cc. water. Heat both solutions and mix equal parts, adding one to the other rather slowly. A clear red or blue suspension results.

To 5 cc. of 1 per cent silver nitrate add very dilute ammonium hydroxide, drop by drop, until a precipitate just disappears. Dilute with 100 cc. of water. Add an equal volume, or less, of tannin solution (0.5 g. in 100 cc. water). Here the tannin reduces the silver oxide to colloidal silver. As with gold, the color varies with the size of particle. Colloidal silver may be cherry-red, brown, or greenish-brown.

Fehling's solution contains a copper complex (tartrate) which is reduced by glucose. Sometimes rather unstable suspensions of cuprous oxide are made with one color by transmitted light and another by reflected light.

6. ***Hydrolysis.*** — If to any dilute solution of ferric chloride hydrochloric acid be added the distinct reddish-brown tint changes to a pure yellow, that of ferric chloride. Ferric chloride is readily hydrolyzed with formation of ferric hydroxide:

$$FeCl_3+3\,H_2O \leftrightarrows 3\,HCl+Fe(OH)_3.$$

It is this colloidal ferric hydroxide that gives solutions their reddish-brown color. Addition of hydrochloric acid drives the reaction to the left (by mass action) and the hydroxide is largely converted into the chloride. Higher temperatures favor hydrolysis. If into a beaker of boiling water a few cc. of 30 per cent ferric chloride be poured a rich red colloidal suspension of ferric hydroxide forms instantly. This is a useful preparation because it is a typical positive colloid and keeps a long time. Hydroxides of aluminum and chromium may be made, but not quite so easily. Other methods are preferred for them.

7. ***Bredig's Electric Arc Method.*** — If two gold wires properly insulated with glass tubes be connected with a 110-volt circuit through sufficient resistance to yield a current of about 10 amperes, and brought close together under water, a small arc forms with violent disruption of the gold. Coarse particles and fine, suspended together, make the water cloudy. A mere trace of sodium hydroxide in the water is a great help, possibly because adsorption of a few hydroxide ions stabilizes the gold. After filtration, a red suspension is obtained. In practice, the simplest manipulation is to bring the wires together rapidly and repeatedly for several minutes.

8. ***Emulsification.*** — One liquid may be dispersed in a second (if they are immiscible) by mere shaking or stirring, but such dispersions, or ***emulsions,*** are temporary, quickly separating into their components. To make emulsions is easy; to keep them is the problem.

Shake water and kerosene together. On standing, the high surface tension of the water drops pulls them into one big drop or layer because of the tendency to expose the least possible surface. By lowering this surface tension of water the emulsion should keep longer. Shake kerosene with a 1 per cent aqueous solution of sodium oleate (a soap which greatly lowers the surface tension of water). A thick, creamy emulsion of drops of oil dispersed in water results and keeps fairly well. As in the case of milk, an emulsion of fat globules in water, etc., a cream slowly separates. This is merely a layer of a richer emulsion above a poorer one.

Now add any acid to this emulsion. It breaks because the added acid destroys the soap, the emulsifying agent. Other emulsifying agents than soaps are possible. Gelatin can be used for kerosene-in-water. Gum arabic is useful, and with the proper liquids cellulose nitrate will serve. Mayonnaise is an emulsion of olive oil in water (or vinegar), with the colloidal albumen of the egg as emulsifying agent.

It is impossible to make a lasting emulsion with two pure liquids — a third substance is necessary as an emulsifying agent and this must be colloidal.

By slowly adding an oil to soapy water with vigorous agitation, Pickering made an emulsion of 99 per cent oil (as separate drops) and 1 per cent water (films between the drops). This emulsion when cut into a cube retained its shape on a flat plate.

There are different theories of the action of emulsifying agents and we are not deciding between them in this chapter. Surface tension lowering is often an important factor, and it is mentioned for that reason.

With the aid of the proper emulsifying agents it is possible to make emulsions of the two types shown in Fig. 90.

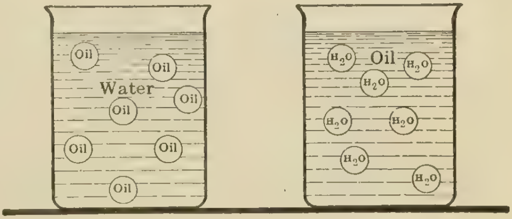


Fig. 90

Dialysis. — Making colloids is one matter, keeping them is another. Since ions of opposite charge tend to coagulate suspensions, a measure of safety should be secured by removing these ions. Fortunately there is a method for accomplishing this, namely, dialysis.

Many membranes such as bladder, intestine, peritoneum, parchment paper, egg skin, and the like, are permeable to water and ions but not to the larger aggregates known as colloids.

To show dialysis quickly, tie a sheet of goldbeater's skin or parchment paper free from pin holes over the mouth of a bottle from which the bottom has been removed by cracking. A wide-mouthed bottle is preferred. Invert the bottle in a large beaker of water and fill with cold, freshly made colloidal ferric hydroxide. This is a mixture of water, colloidal aggregates of ferric hydroxide and the ions of hydrochloric acid. The smaller ions and molecules pass out through the membrane and if the outer water be frequently changed they are almost completely removed, leaving only ferric hydroxide suspended in water. The last trace of ions is often difficult to remove and may even be necessary to the stability of the colloid. A bag of parchment paper, bladder, goldbeater's skin or collodion may be filled with the suspension to be dialyzed and suspended in a beaker of water as in Fig. 91.

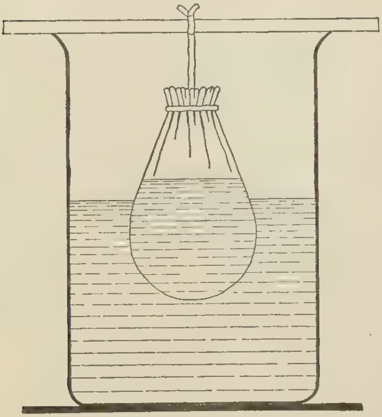


Fig. 91

In trying the experiment with colloidal ferric hydroxide samples of the dialysate (corresponding to filtrate) should be removed in a few minutes, and tested with silver nitrate. The passage of chlorides through the membrane is very rapid.

Classification. — Examples of the ***suspensoid state*** are found in colloidal gold, silver, arsenic sulfide and nearly all the colloids mentioned above. These are easily coagulated by very small quantities of electrolytes and have a viscosity but little more than that of the liquid in which they are dispersed. Water containing twenty per cent of barium sulfate in suspension is stirred about as easily as water alone.

Examples of the ***emulsoid*** state are found in water suspensions of gelatin, agar, glue, starch paste, soaps, egg albumin, silicic acid, and the like. These are coagulated only by relatively large quantities of salts and are extremely viscous. A one per cent suspension of agar in water is a solid jelly at room temperatures as in a one per cent suspension of sodium stearate soap.

If evaporated to dryness, or coagulated, the suspensoids are *irreversible*, that is, they can't be suspended again. The emulsoids after evaporation are easily thrown into suspension again and so are *reversible*. Of course there are gradations between these two states.

Adsorption. — A cube 1 cm. on edge has a surface of 6 sq. cm. If subdivided into smaller cubes, each only 100 $\mu\mu$ on edge, the total surface is 600,000 sq. cm. and there are 10^{15} particles. If further subdivided into the collodial realm of 10 $\mu\mu$ on edge, the total surface becomes 6,000,000 sq. cm. In number the particles have grown from one to 10^{18}. This vast increase of surface magnifies all surface influences. Adsorption has already been mentioned as a holding of various substances to specific surfaces. The adsorptive power of a definite weight of carbon, for example, may be vastly increased by subdividing the carbon. Bone charcoal is used in sugar refineries to decolorize sugar syrup by adsorption of coloring matter. A sugar refiner buys this carbon for its surface, so size of particle means something to him.

Bacteria are adsorbed by sand filters. It cannot be a sieve action, for bacteria are much smaller than the spaces between sand grains. Potassium salts and soluble phosphates as well as nitrates are adsorbed on the surface of the humus particles of soils. Otherwise the fertilizers would be washed away with the first hard rain.

Charcoal made from cocoanut shells was used in our gas masks to adsorb most of the poison gases. Without an adequate adsorbing powder of this type an army to-day would be almost helpless.

In an empty flask pour two or three cc. of concentrated hydrochloric acid. Then add an equal amount of concentrated ammonium hydroxide. The flask fills with fumes of ammonium chloride. Pour in some water and shake. Although ammonium chloride is very soluble the white fumes are slow to dissolve. The reason is that each little solid particle adsorbs a film of air which keeps the water away from the ammonium chloride.

The cleansing action of soap is an adsorption phenomenon. Soap in water is colloidally dispersed and so exposes great surface. It has a strong adsorptive power towards dirt, and carries dirt away on its surfaces. If soap did not adsorb dirt more strongly than does linen, for example, the dirt would remain on the linen. The older theory of cleansing action was that soap is hydrolyzed to form sodium hydroxide as needed and that the alkali does the cleaning. This is absurd, for the concentration of alkali obtained in the hydrolysis of soap is too minute to have any value in cleansing. And alkali in any concentration has no effect in removing mineral oils. To round out the modern theory we should state that soap, by lowering surface tension of water, emulsifies the grease or oils that so often cause the dirt to stick on the skin or fabrics and thus allows the dirt to be washed off. But it is to be noted that this emulsification requires rubbing to disintegrate the oil or grease.

Adsorption is relatively greater from very dilute solutions of the substance adsorbed than from more concentrated solutions and does not obey the law of definite proportions.

Coagulation. — Suspensions coagulate when the causes of their stability are removed. If the colloidal aggregates coalesce and become large enough, they get beyond help from Brownian movement and settle. The destruction of protective films may lessen stability by allowing particles to coalesce. But in general the suspensoids are coagulated by addition of oppositely charged ions. The bivalent ions are far more than twice as effective in precipitating powers than the univalent ions, while the trivalent ions are hundreds of times as effective. This enables us to recognize the charge on a colloid.

Test the precipitating power of 0.05 molar solutions of $NaCl$, Na_2SO_4, Na_2HPO_4, $BaCl_2$ and $AlCl_3$ on such typical positive and negative colloids as ferric hydroxide and arsenic sulfide. Add the salt solutions slowly. If the trivalent phosphate ion has the highest precipitating power the colloid must be opposite in charge, namely, positive. If, on the other hand, the trivalent aluminum ion has greatest precipitating power, the colloid must have an opposite charge, namely, negative.

Oppositely charged colloids may coagulate each other if mixed in equivalent quantities. Emulsoids are coagulated by excessive amounts of salts, sometimes by heat, by shaking and by nitric acid.

Protective Colloids. — Mix equal quantities of 0.1 N silver nitrate and 0.1 N potassium bromide. A curdy precipitate forms. Now try the experiment again with solutions containing one per cent gelatin. A suspension results. Gelatin is a protective colloid and forms a film around the separate particles of silver bromide so they cannot touch each other and coalesce. Gold reduced in the presence of gelatin is much more stable — harder to coagulate than without gelatin. In fact the suspensoid, or irreversible colloid particles, when covered by films of gelatin, act as if they were solid particles of gelatin — become reversible. Collargol is a medicinal form of colloidal silver which can be suspended in water. It was protected in preparation by gelatin or some other good film former. These protective colloids are all organic compounds, hence the order to destroy all organic matter in qualitative analysis. Desired precipitations might easily be prevented by such organic matter.

Gels and Jellies. — On cooling a hot water suspension or solution of sodium stearate soap a translucent solid called a jelly results if the soap concentration is about one per cent or more. A one per cent hot gelatin solution "sets" to a jelly on cooling as does a two per cent agar solution. The usual "egg preserving" water glass (sodium silicate) diluted to a specific gravity of about 1.12 and then poured into an equal volume of 2 N acetic acid sets rather soon to a slightly opaque jelly of silicic acid. When these proportions do not secure the expected result they should be varied slightly. In the case of the water glass if the mixture be placed in a dialyzer at once silicic acid will pass through the membrane. Later it will not do so and still later a jelly forms. Of course this can be formed only with a slow-setting gel. This shows a gradual growth in size of particle from the molecular to the colloidal.

There is some sort of a regular structure, filaments, honeycomb or flattened coalescing spheres of highly hydrated material in the aqueous jelly. Some authorities think that gels and jellies are composed of drops of a less hydrated material surrounded by a continuous mesh of more hydrated material. At any rate electrolytes and many other substances diffuse through jellies with astonishing ease.

Gels are irregular lumpy masses of the jelly nature. Stirring a silicic acid jelly as it sets results in a lumpy gel. The term *hydrated* applies only to water systems. Jellies made from other liquids are known and they are described by the broader term *solvated.*

The highly hydrated tissues of the body are gels. Protein is capable of swelling in water, of taking up the water, especially in the presence of a little acid or base. Accumulation of acid in the body through disease may show its effects in undue swelling (œdema) of certain tissues. Without doubt the colloid chemistry of protein is of great importance in medicine.

Fruit jellies afford a familiar example of hydrated tissues. Pectin (a carbohydrate found in most fruits), sugar and acid (with water) are essential to the formation of fruit jellies. Color and flavor are incidental. Apples are so rich in pectin that if this constituent be lacking in a given fruit, apples may be added or the white rind of citrus fruits. When acid is lacking in the fruit, sour grapes or lemon juice are often added.

"*Solid Alcohol*" fuel may be prepared by quickly mixing about 85 volumes of 95 per cent alcohol with 15 volumes of a saturated aqueous solution of calcium acetate. The mixture "sets" to a solid jelly instantly. Cubes of it may be burned under a chafing dish.

Soaps. — The alkali salts of oleic acid and stearic, palmitic and the other fatty acids are the soaps we commonly use. These soaps hydrate heavily. As a result commercial soap, although sold in solid cakes, contains a surprising amount of water. Soap flakes are dryer. However, the alkali salts of the unsaturated acids, such as oleic, hydrate much less than those of the saturated acids, such as palmitic and stearic. In other words, a cake of soap made from cottonseed oil (liquid unsaturated fats) contains less water than a similar cake made from hydrogenated cottonseed oil (now saturated with hydrogen). Soaps of the type of sodium oleate (*genuine* Castile) disperse better in cold water than do soaps of the saturated sort such as sodium stearate or palmitate and therefore cleanse better. Naturally sodium oleate is preferable for toilet use. In the very hot water of laundries sodium stearate and the rest of its class are at their best. Soaps of calcium, magnesium, lead, and of all but the alkali metals hydrate very little, do not disperse well in water, and are therefore "insoluble." They are useless for cleansing.

Applications of Colloid Chemistry. — All the sciences, even astronomy dealing with colloidal dust of comets' tails, are dependent on colloid chemistry for their full development. Physics with its surface energy problems, geology with diffusion through gelatinous silicic acid and fine powders, biology with hydrated plant and animal tissues, medicine with the study of hydration and diffusion in body tissues and peptization by digestive juices, engineering with countless colloid problems to solve — all eagerly watch the rapid growth of the young science of colloid chemistry.

Glues and adhesives in general are colloids, many of them of protein nature. A water-resistant glue is desperately needed in order that large timbers may be built of laminated smaller strips glued together. We can build such timbers now, but the glue ultimately weakens in moist air. With the rapid depletion of our forests this problem will become acute.

Lubrication deals with powerful adsorption of films on the bearing surfaces. The greases are emulsions of a little water in soap-oil jellies. Acheson's "oildag" is a suspension of colloidal graphite in oil and has high value as a lubricant.

A great increase in the amount of copper and zinc recovered from their sulfide ores was secured by the flotation process. An oily froth by selective "wetting," floats the finely grouped particles of the mineral sulfides, while the waste rock, selectively "wetted" by water, sinks. Over 60,000,000 tons of ore were "floated" in 1918.

The tanning of leather consists essentially in making one colloid, the raw hide, insoluble by the use of another, tannin or chromium oxide. The textiles including artificial silk involve a detailed study of filaments, even of hydration. Dyeing is in part an adsorption of coloring matter by filaments. Rubber latex direct from the tree is a milky emulsion of rubber with a protein as the emulsifying agent. This protein is coagulated by smoking or other methods of curing. In vulcanizing raw rubber, sulfur is adsorbed.

The enormous ceramic industry deals largely with the colloidal nature of clays. To mention a single point, wet clays to be poured into molds for making heavy porcelain objects must carry a good deal of water. But in drying and baking this wet clay there is great shrinkage and distortion. Obviously if the desired fluidity could be secured with less water there would be less warping. A very little sodium hydroxide makes this possible. Adsorption of hydroxide ions peptizes the clay so that it flows as well into molds as if it contained much more water.

Cooking is a change in the colloidal structure of food. Milk itself is an emulsion. The production of food on the farm depends on the colloidal condition of the soil.

The alloys we use are partly suspensions of solid-in-solid. Wood, paper, clothing, glass, cement, enamels, candles, paints, varnishes, celluloid, inks, asphalt, cheese, photographic films, — these and many more are colloidal. The field is vast.

If, in later years, the student wishes to read more along these lines he will enjoy:

An Introduction to the Physics and Chemistry of Colloids, by Hatschek. P. Blakiston's Sons & Co., Philadelphia.

Colloid Chemistry, by Jerome Alexander. D. Van Nostrand Co., New York.

The Chemistry of Colloids, by Zsigmondy. John Wiley & Sons, New York.

Colloid Chemistry, by W. D. Bancroft. McGraw-Hill & Co., New York.

Fats and Fatty Degeneration, by Martin Fischer. John Wiley & Sons, New York.

Theoretical and Applied Chemistry, by Ostwald-Fischer. John Wiley & Sons, New York.

CHAPTER XXVI

THE METALS

We have been taught that the "metals are elements whose oxides react with water to form bases." This suggests the name "base-forming elements." But such a definition is not very exact, as aluminum hydroxide is just as acidic as basic and the higher hydroxides of some metals are distinctly acidic. Some writers prefer to state that a metal is the only element forming simple positive ions. The metals and non-metals really merge. However, the above definitions are approximately correct and are useful.

Exercise 1. — What is formed when Mn_2O_7 reacts with water?

Physical Properties. — A characteristic property of metals is their *metallic luster.* They reflect light well when polished. Yet so do some mineral sulfides and tellurium. They are all white in the massive form except gold and copper. Curiously enough nearly all of them are black in powdered form. When subdivided to colloidal dimensions and properly suspended, various colors are observed as red, blue and green for gold.

Most metals are *malleable,* capable of being hammered or rolled into thin sheets. The most malleable are gold, silver, copper, tin, platinum, and lead. Gold leaf has been hammered to a thickness of 0.0001 mm. and was then almost transparent at 200°–500°. Malleability changes with temperature. Iron, as is well known, is most easily rolled at red heat. Zinc shows maximum malleability at 100°–150° and is actually brittle at 205°. Arsenic, antimony and bismuth, being more like the non-metals, are brittle.

Tenacity is measured by the number of kilograms a wire 1 sq. mm. in cross section will sustain without breaking. This is for iron 62, copper 42, platinum 34, silver 29, gold 27, aluminum 20, zinc 5 and lead 2. Many metals may be drawn out into very fine wires. For example, platinum wire only 0.00008 mm. in diameter has been made.

High *electrical conductivity* distinguishes the metals from the non-metals. On the arbitrary scale of 100 for silver, the relative conductivity of a few common metals are given.

Silver	100	Zinc	29.02
Copper	99.95	Tin	12.36
Gold	77.96	Lead	8.32
Aluminum	66.00	Nickel	7.89
Cadmium	32.72	Mercury	1.61

It is a fortunate thing for our electrical industries that copper, almost unsurpassed as a conductor, is plentiful. Aluminum, with two thirds its conductivity (for equal diameter of wire) becomes a competitor in the electrical industry whenever the price of copper rises unduly. Silver is out of the question on account of its cost and scarcity. The conductivity of metals increases with fall in temperature, but the conductivity of electrolyte solutions increases with rise in temperature.

The melting points of metals vary widely. The figures given below were issued by the United States Bureau of Standards in 1913.

Mercury	−38.7°	Silver	661.0°
Potassium	+62.3°	Calcium	810.0°
Sodium	97.5°	Barium	850.0°
Lithium	186.0°	Arsenic	850.0°
Tin	232.0°	Gold	1063.0°
Bismuth	271.0°	Copper	1083.0°
Cadmium	321.0°	Manganese	1260.0°
Lead	327.0°	Nickel	1452.0°
Zinc	419.0°	Cobalt	1478.0°
Antimony	630.0°	Chromium	1520.0°
Magnesium	651.0°	Iron	1530.0°
Aluminum	659.0°	Platinum	1755.0°

Boiling points (metals boil, at least in the arc) and melting points do not run parallel. Mercury 357°, sodium 700°, zinc 950°, lead 1525°, iron 2450°, tin 2270°, copper 2310° and aluminum 1800° show us typical boiling points.

All metals except mercury are solid at ordinary temperatures. All of *density* less than 5 are called *light metals* and the others *heavy metals.* Osmium 22.48, platinum 21.5, gold 19.3, mercury 13.6, lead 11.38, silver 10.31, tin 7.29, zinc 7.15, calcium 1.83, and lithium 0.59 suggest some interesting variations in density.

In *specific heat* (the number of calories required to raise 1 g.

one degree) the metals vary from lithium 0.9408, aluminum 0.2143, iron 0.1138 and copper 0.0952 to antimony 0.0523.

EXERCISE 2. — What is the law of Dulong and Petit?

Metals dissolve in each other (to some extent) forming *alloys* and yet some alloys are real compounds of the metals. For a better discussion of alloys read page 273. Amalgams are alloys containing mercury.

When a mass of molten metal is cooling, the liquid portion may be poured off. This is conveniently done with antimony and bismuth. Usually the remaining solid is crystalline (cubic system).

That the metals are monatomic is indicated by their vapor density and the melting points of the alloys. Small amounts of added elements greatly modify some metallic properties. Iron containing a few tenths of one per cent carbon is steel. Gold containing one part in 2000 of lead is very brittle. Iron, nickel, and cobalt are the most magnetic elements.

EXERCISE 3. — Which would give off the greater amount of heat on cooling, 1 K. of liquid water or 1 K. of aluminum?

Chemical Properties.— A characteristic property of metals is their ability to form simple positive ions. They may be found also in negative ions, but not alone. The permanganate ion (MnO_4) illustrates this point.

Metallic oxides and hydroxides as a class are basic. At least one halide of each metal is not completely hydrolyzed. Halides of the non-metals (chlorides of phosphorus, for example) are completely hydrolyzed. Carbon tetrachloride is an exception.

The lighter metals are more active (see Electromotive Series), combining with many elements. The heavier metals are less active and their oxides and chlorides, for example, are less stable.

Occurrence. — Very few metals occur free or *native* and these are the less active ones — gold, silver, the platinum group, copper, mercury, bismuth, antimony, and arsenic.

The important *oxides* are those of iron, tin, copper, aluminum, zinc and manganese.

The *sulfide* ores smelted for the metals are those of copper, zinc, cadmium, lead, antimony, cobalt, nickel and molybdenum. In addition to these are iron pyrites, used as a source of sulfur dioxide and ores containing more than one sulfide.

The *carbonates* of metallurgical importance are those of iron, lead, copper and zinc, but the carbonates of calcium, barium, strontium and magnesium are important as sources of the oxides and other salts.

Halogen ores are known as the salt deposits at Stassfurt and elsewhere, including chlorides and bromides of sodium, potassium, and magnesium. Some fluorspar (CaF_2) and cryolite ($3\ NaF.AlF_3$) are also found as ores.

The insoluble *sulfates* of lead, barium, calcium and strontium are reasonably common, as are some solid sulfates.

The *silicates* are seldom used as a source of any metal, but have their uses in ceramics. However, aluminum can be made from clay, at considerable cost, and it is possible that some time this will be the chief source of that metal.

Extraction from the Ores. — Metallurgy is the art of extracting a metal from its ores. Where the metal occurs free, merely mixed with rock, heating in a furnace, to melt away either the metal or the rock, is adequate. Sometimes a substance, usually lime or sand, is added to react with impurities, forming very fusible double silicates which are separated as a "slag." Native zinc and mercury are easily distilled away from the residues.

Oxides are usually reduced by hot coke. In making pig iron, this principle is of enormous importance as the oxide is the chief ore of iron. Some oxides such as those of aluminum, magnesium, calcium and the chromium group are not reduced by carbon except at the temperature of the electric furnace. Unfortunately this method produces carbides as an impurity.

Aluminothermy is a modern process for preparing carbon-free metals from their oxides. Ignited powdered aluminum is a powerful reducing agent.

$$3\ Mn_3O_4 + 8\ Al \rightarrow 4\ Al_2O_3 + 9\ Mn.$$

If mixed oxides are used, alloys may result. Many very important ferro-alloys such as "ferrochrom," "ferromanganese," etc. are prepared in this way. The comparative cheapness of aluminum has made this process (invented by the German chemist, Goldschmidt) very important, not merely in preparation of metals but in welding.

Preparation of Manganese by the Goldschmidt Method. — The reaction between aluminum powder and manganese dioxide is too violent, so it is safer to use Mn_3O_4 prepared by heating the dioxide to a red heat. From 500 g. of the dioxide about 420 g. mangano-manganic oxide is prepared. In a Hessian crucible more than large enough to hold the mixture put the oxide well mixed with 140 g. of coarse aluminum powder. It is best to add at first, only three or four spoonfuls of the mixture. It is covered with 5 g. ignition powder (one part aluminum to 10 parts barium peroxide) which is heaped up in the middle. A strip of magnesium ribbon is inserted in the powder. Gloves and colored glasses protect the operator, while asbestos sheets protect the desk top. The crucible rests on a pan of sand. When the magnesium ribbon is ignited the reaction starts. The remainder of the charge is added, not too rapidly, from an iron spoon. The molten material (3000°–3500°) often cracks the crucible. The slag is aluminum oxide.

Carbonates are roasted to convert them into oxides which are then reduced with hot coke. Hydroxides, on roasting, also become oxides. Roasted sulfides yield sulfur dioxide and the oxide of the metal.

Halides were once reduced to the metal by heating with metallic sodium. At one time aluminum was prepared this way and a sudden expansion of the sodium industry was in process. Just at this critical stage of development, Hall invented the electrolytic method of preparing aluminum — and the sodium industry was almost ruined:

$$AlCl_3 + 3\ Na \rightarrow 3\ NaCl + Al.$$

Electrolysis of fused salts now furnishes us with calcium, sodium, potassium and such metals as are difficult to prepare by other methods. A solution of aluminum oxide in melted cryolite is electrolyzed to produce aluminum.

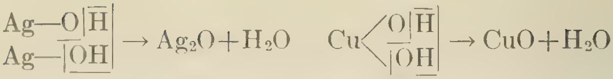
EXERCISE 4. — How is antimony separated from its sulfide?

Preparation of Compounds of the Metals. — Although salts are the most numerous compounds of the metals, the oxides and hydroxides are important.

Oxides may be prepared in at least four ways:

1. Direct union of the elements, usually at high temperature.

2. Heating hydroxides with loss of water. Silver hydroxide decomposes at ordinary temperatures, copper hydroxide quickly at 100°, and all hydroxides (except those of the alkali metals and barium hydroxide) at temperatures easily obtained.



$$\left.\begin{array}{l}Ag—O|\overline{H}\\ Ag—|\underline{OH}\end{array}\right| \rightarrow Ag_2O+H_2O \qquad Cu\begin{array}{l}\diagup O|\overline{H}\\ \diagdown |\underline{OH}\end{array}\Bigg| \rightarrow CuO+H_2O$$

3. Heating any carbonates except those of the alkali metals:

$$CaCO_3 \rightarrow CaO+CO_2.$$

4. Heating most nitrates. The alkaline nitrates yield nitrites on heating:

$$2\,Cu(NO_3)_2 \rightarrow 2\,CuO+4\,NO_2+O_2.$$

Hydroxides are made in two ways:

1. Union of an oxide with water:

$$CaO+H_2O \rightarrow Ca(OH)_2.$$

2. Double decomposition between a soluble base (such as sodium hydroxide) and a salt of the metal concerned:

$$NiCl_2+2\,NaOH \rightarrow 2\,NaCl+Ni(OH)_2.$$

Since nearly all the hydroxides of the heavy metals are insoluble, filtration and thorough washing of the precipitate is all that is necessary to give a good product.

The preparation of *salts* may be illustrated with the chloride.

1. Direct union of the elements:

$$2\,Na+Cl_2 \rightarrow 2\,NaCl.$$

2. Reaction of the acid with the metal (with exceptions indicated by the Electromotive Series):

$$Zn+2\,HCl \rightarrow H_2+ZnCl_2.$$

3. Reaction of the acid with an oxide of a metal:

$$Cu\boxed{O+2\,H}Cl \rightarrow H_2O+CuCl_2.$$

4. Reaction of the acid with an hydroxide of a metal:

$$Cu\boxed{(OH)_2+2\,H}Cl \rightarrow 2\,H_2O+CuCl_2.$$

5. Reaction of the acid with the carbonate of a metal:

$$Cu\boxed{CO_3+2\,H}Cl \rightarrow CuCl_2+H_2CO_3.$$
$$H_2CO_3 \rightarrow H_2O+CO_2$$

6. Reaction of the acid with a sulfite or sulfide of a metal or any reaction based upon the volatility of one product for its completion:

$$CaSO_3+2\ HCl \rightarrow CaCl_2+H_2SO_3$$

$$H_2SO_3 \rightarrow H_2O+SO_2 \uparrow$$

$$FeS+2\ HCl \rightarrow FeCl_2+H_2S \uparrow$$

7. Double decomposition depending on insolubility of one product for its completion. Unless one product escapes as a gas (Method 6) or is precipitated out of good contact, an equilibrium results with a mixture of four substances present. In preparation work we want reactions to proceed to completion and we want a product unmixed with other substances (except water which can later be removed by simple evaporation). Precipitates may be filtered, washed and dried:

$$BaCl_2+Na_2SO_4 \rightarrow 2\ NaCl+BaSO_4 \downarrow$$

Some salts are prepared by special methods. Nitrites of the alkali metals are made by simple heating of the nitrates. Carbides (such as CaC_2, Al_4C_3) are formed in the electric furnace from the action of excess carbon on a metallic oxide. Carbonates may be prepared by passing carbon dioxide into solutions of the bases, but this is equivalent to the use of carbonic acid. Reaction of any salt with a soluble carbonate ($BaCl_2+Na_2CO_3 \rightarrow 2\ NaCl+BaCO_3$) yields the carbonate desired. Insoluble compounds of the metals are sometimes fused with sodium carbonate to secure carbonates of the metals in question ($BaSO_4+Na_2CO_3 \rightarrow BaCO_3+Na_2SO_4$). They are also prepared by contact of carbon dioxide with the dry oxide or hydroxide. Probably a trace of moisture is needed. The air slaking of lime is an example:

$$CaO+CO_2 \rightarrow CaCO_3.$$

This looks like the union of anhydrides of acid and base. The same union is observed on heating sand with metallic oxides:

$$CaO+SiO_2 \rightarrow CaSiO_3.$$

In glass making silicates are prepared by the attack, not of an acid, but of an acid anhydride on a carbonate:

$$CaCO_3+SiO_2 \rightarrow CaSiO_3+CO_2.$$

Sulfides are made by direct union of sulfur and the hot metals or by reaction of solutions of hydrogen sulfide or any soluble sulfide with a salt or by reduction of a sulfate:

$$BaSO_4 + 2\ C \rightarrow BaS + 2\ CO_2.$$

Double Salts. — When certain salts are mixed in proper proportions and the solution concentrated slowly, crystals appear containing both salts in a very definite proportion. These are called double salts. The alums are good examples:

$$K_2SO_4 + Al_2(SO_4)_3 + 24\ H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3.24\ H_2O.$$

In dilute solution these double salts yield the simple ions of their constituent salts. However some salts on mixing form compounds which do not yield all the simple ions again. These are called *complex salts:*

$$Fe(CN)_2 + 4\ KCN \rightarrow K_4Fe(CN)_6,$$

$$K_4Fe(CN)_6 \leftrightarrows 4\ \overset{+}{K} + \overset{----}{Fe(CN)_6}.$$

The potassium ferrocyanide mentioned here yields no simple iron ions, but instead the complex ferrocyanide ion. A similar complex ion of cadmocyanide breaks down to a slight extent, yielding some simple cadmium ions, but much of the complex still remains.

Solubility of the More Common Salts in Water

All *nitrates* are soluble. The nitrate of bismuth is hydrolyzed considerably, with formation of a precipitate, but an excess of nitric acid prevents this.

All *chlorides* are soluble except those of silver, lead and univalent mercury. Lead chloride is slightly soluble in cold and very soluble in hot water. Cuprous chloride is almost insoluble.

All *sulfates* are soluble except those of lead, barium, strontium and calcium. To be exact, calcium sulfate is slightly soluble.

All *hydroxides* are insoluble except those of sodium, potassium, ammonium, barium, calcium and strontium. Calcium hydroxide is only slightly soluble.

All *sulfides* are insoluble except those of sodium, potassium and ammonium. Those of the calcium family are hydrolyzed completely by water.

All *carbonates*, *phosphates* and *silicates* (of normal salts) are insoluble except those of sodium, potassium and ammonium.

Comparison of Metals and Non-metals

The following résumé of the properties of metals and non-metals (taken from Mellor's *Inorganic Chemistry*) is very useful for study at this time.

Metals	Non-metals
1. Form basic oxides.	1. Form acidic oxides.
2. Generally dissolve in mineral acids giving off hydrogen.	2. Do not usually dissolve easily in mineral acids.
3. Either form no compounds with hydrogen or form unstable compounds — usually nonvolatile.	3. Form unstable compounds with hydrogen — these are usually volatile.
4. Solid at ordinary temperatures (excepting mercury).	4. Gases, liquids, or solids at ordinary temperatures.
5. Usually volatilize only at high temperatures.	5. Excepting carbon, boron, and silicon, the non-metals are either gaseous or solid at low temperatures.
6. When in bulk the metals reflect light from polished or freshly cut surfaces.	6. Do not usually reflect light very well.
7. Specific gravity is generally high.	7. Specific gravity is generally low.
8. Good conductors of heat and electricity.	8. Bad conductors of heat and electricity.
9. More or less malleable and ductile.	9. Malleability and ductility are not well defined.

CHAPTER XXVII

THE ALKALI METALS

Element		Atomic Weight	Density	Melting Point	Boiling Point	Atomic Volume = $\frac{\text{At. Wt.}}{\text{Density}}$
Lithium	(Li)	6.94	0.534	186.0°	1400.0°	13.1
Sodium	(Na)	23.00	0.971	97.0°	877.5°	23.7
Potassium	(K)	39.10	0.862	62.5°	700.0°	45.4
Rubidium	(Rb)	85.45	1.532	38.5°	696.0°	55.8
Cæsium	(Cs)	132.81	1.87	26.5°	670.0°	71.0

This group of elements, as shown by its position in the periodic system, is strongly metallic. The alkali metals are the most active of all metals, reacting violently with water, and hence are not found free in nature. In the laboratory these metals must be kept under oil to exclude moisture and oxygen. Their hydroxides are the strongest bases. The elements are soft with a silvery luster, quickly tarnishing in the air with formation of layers of oxide, hydroxide and carbonate. All the elements of this group are obtained by electrolysis of their fused salts or hydroxides or by reduction of oxides, carbonates or hydroxides. The valence is uniformly one throughout the group.

In some respects sodium is different from the rest of the group, but in general, density, melting point and other properties change regularly with atomic weights within the group. Nearly all the salts are white and very few are insoluble. For most uses the cheaper sodium compounds can be substituted for potassium compounds.

The hypothetical metal, ammonium (NH_4), in a way belongs to this group, although it is known only in combination.

Exercise 1. — If you should discover a new metal, univalent and strongly base-forming, with atomic weight about 62, what would be its approximate density, melting point, boiling point and atomic volume?

LITHIUM

Lithium is far from plentiful and its compounds have few uses. Its existence was first recognized by Arfredson in 1817, but it was not isolated until prepared by Bunsen in 1858. Its compounds occur in igneous rocks in very small amounts. Traces are found in soils and are adsorbed by tobacco and the sugar beet. Some mineral waters contain such compounds and as "lithia waters" are taken for rheumatism. Since lithium urate is soluble, it was supposed that the accumulation of uric acid in the joints could be dissolved by lithium salts. This supposition is supported neither by physical chemistry nor by medical experience. Rheumatism is caused by an infection and the presence of uric acid is merely a symptom. However, no harm is done by drinking plenty of water, lithia or otherwise.

There are a few lithium minerals worth noting. Lepidolite is found in California and spodumene and amblygonite in South Dakota.

Lithium is the lightest solid known and one of the most active metals. It unites with nitrogen at ordinary temperatures:

$$6\ \mathrm{Li} + \mathrm{N_2} \rightarrow 2\ \mathrm{Li_3N}.$$

Lithium salts are used in medicine, and the carbonate in the Edison storage cell. Lithium carbonate and phosphate are but slightly soluble, rather a surprising fact in view of the great solubility of the salts of the other alkali metals. Lithium compounds are easily recognized by the color they impart to the flame.

SODIUM

Occurrence. — There is slightly less sodium than potassium in the earth's crust, but most sodium minerals are soluble, while soluble potassium minerals are scarce. Sodium chloride is the starting point for most of our prepared sodium compounds. There are also important deposits of sodium nitrate, sodium sulfate, sodium carbonate, borax and albite feldspar.

Preparation. — Sir Humphry Davy was the first to prepare sodium. He electrolyzed moist sodium hydroxide and collected the metal at the cathode. In the same year (1807) he made potassium from its hydroxide. The high cost of electricity for many years hindered the commercial development of Davy's discovery. During this period the metal was prepared by reduction of the carbonate or hydroxide:

$$Na_2CO_3 + 2\ C \rightarrow 3\ CO + 2\ Na.$$

With cheap electricity Davy's method was revived, in modified form. Castner's method, now much used, is to electrolyze fused sodium hydroxide in an iron vessel with the cathode under a bell or inverted iron box (Fig. 92). The metal floats to the surface under this bell and is protected from the air by the hydrogen which is also liberated at the cathode. From time to time the hydrogen escapes by lifting the lid of the bell. Oxygen is released at the anodes. A wire gauze keeps the drops of sodium in the cathode compartment. Good commercial practice calls for a temperature as close to the melting point of the hydroxide (300°) as possible. At 325° the sodium is lost by reaction with the hydroxide, while at 300° the yield is good:

$$2\ Na + 2\ NaOH \rightarrow H_2 + 2\ Na_2O.$$

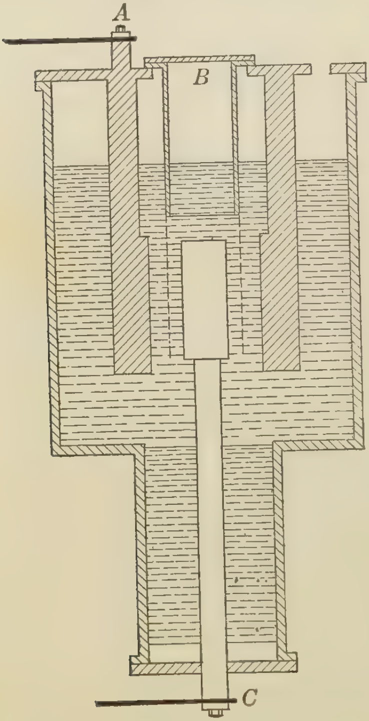


FIG. 92

Properties. — Sodium is silver-white, soft, and lighter than water. It melts at 97° and boils at 877.5°. The vapor is blue and its solution in anhydrous liquefied ammonia is also blue. Like the similar blue potassium solution, this remarkable liquid conducts electricity *without decomposition*. The beautiful blue color of some specimens of rock salt is due to minute particles of the free metal dispersed in the salt (a solid colloidal suspension). Sodium is very active, reacting violently with water. In a somewhat similar way it displaces hydrogen from alcohol:

$$2\,H_2O+2\,Na \rightarrow 2\,NaOH+H_2,$$
$$2\,C_2H_5OH+2\,Na \rightarrow 2\,C_2H_5ONa+H_2.$$

It unites with oxygen in the cold and burns if heated in oxygen or air. With the halogens reaction readily occurs.

Sodium amalgam is a solution of sodium in mercury (really an alloy). With plenty of sodium the solution is a solid. Its action on water is moderated by the mercury, so the alloy is a useful reducing agent. An alloy of lead and sodium is quite similar. Most of the sodium now made is used to prepare the peroxide and cyanide.

Sodium Chloride. — Fortunately for the human race this necessary mineral is plentiful in most countries. Two thirds of the solid in sea water is common salt, and some is still obtained from this source by solar evaporation. Great beds of solid salt are found at Stassfurt, at Salzburg, and in several districts of the United States. Dried-up lakes have left easily mined deposits. Deep beds are usually tapped with wells and, if necessary, water introduced to form a brine. This brine, or any natural brine, is pumped up and concentrated. Some brines contain magnesium chloride and bromide. On too great concentration these begin to crystallize from the "bitter liquor." As a rule this bitter water is treated with sulfuric acid and sodium chlorate to recover the bromine. Some magnesium chloride contaminates even table salt. It is this very soluble and hygroscopic impurity that makes salt "cake" in the table shakers. Starch is often added to coat each particle. Baking soda ($NaHCO_3$) is used also to convert the magnesium chloride into the insoluble carbonate.

Salt crystallizes in cubes with hollow faces. It melts at 801° and volatilizes at high temperatures. As the chief source of sodium compounds, as a food preservative and as an essential article of diet sodium chloride is of major importance.

In 1919 the United States alone produced 7,000,000 tons of salt. The great producing states are New York, Michigan, Ohio, Kansas, Louisiana, Texas, Utah, West Virginia and California.

Sodium Bromide and Sodium Iodide. — These salts resemble the chloride in many respects. Both are used in medicine and in photography. They are prepared by the action of bromine or iodine on sodium hydroxide or by adding sodium carbonate to a mixture of iron filings and the free halogen. Iron filings and iodine in water form a solution of ferrous iodide, FeI_2. To this solution is added one half as much iodine as before, thus forming a higher iodide, Fe_3I_8. Addition of sodium carbonate precipitates the iron and leaves sodium iodide in solution:

$$Fe_3I_8+4\ Na_2CO_3+4\ H_2O \rightarrow Fe_3(OH)_8+4\ CO_2+8\ NaI.$$

Sodium Fluoride. — This compound differs from the chloride, bromide, and iodide in being only moderately soluble. It has a use as a preservative in distilleries, yeast factories and in checking decay of wood.

Sodium Hydroxide, NaOH. — This important substance is a white brittle solid. It is very soluble in water and is quite deliquescent. Sticks exposed to the air rapidly take up water and carbon dioxide. For this reason it is often used to absorb carbon dioxide in analysis and as a drying agent. To purify the hydroxide it is sometimes dissolved in alcohol. Any carbonate present remains undissolved. The purest product, however, is prepared by cautious addition of sodium to water. There are obvious objections to this method. It has been made commercially by treating boiling soda solutions with slaked lime in some excess:

$$Na_2CO_3+Ca(OH)_2 \rightarrow CaCO_3+2\ NaOH.$$

The precipitated calcium carbonate is filtered off and the filtrate concentrated. The modern method, however, is the electrolysis of sodium chloride solutions. The amalgamation method is represented by Castner's process. In a three-compartment cell the graphite anodes are placed in the outer compartments, where chlorine is released. Mercury, forced to move along the floor of the entire cell, acts as cathode and receives the deposit of metallic sodium. The amalgam formed reacts with water in the middle compartment to form sodium hydroxide. By a modification of this process an iron cathode is suspended in the middle compartment. The caustic solution of the inner chamber is drawn off at intervals and evaporated. Salt water is continuously introduced into the anode chambers.

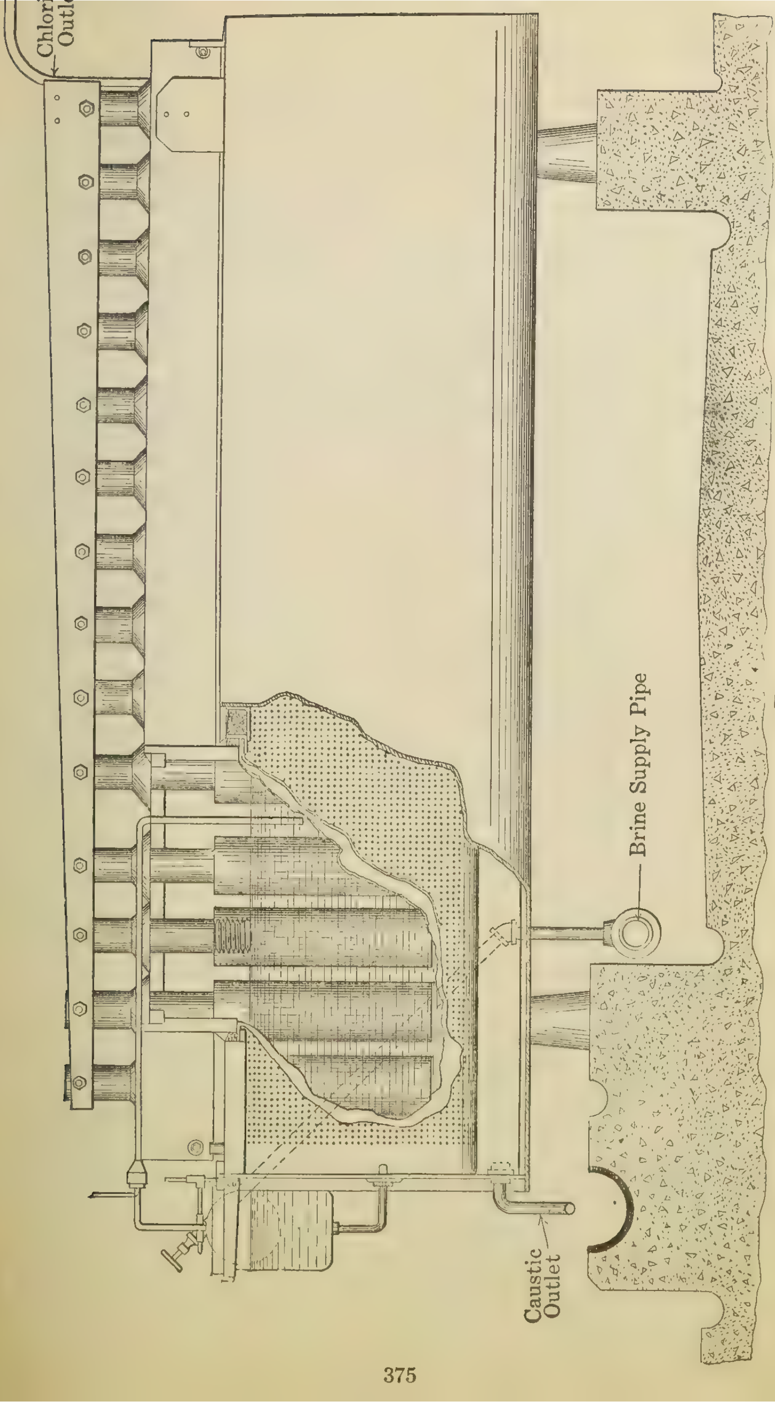


FIG. 93

The Nelson cell (Fig. 93 and Fig. 94) is used more than any other. It belongs to the diaphragm type. The graphite anodes are separated from the cathode, a perforated steel plate, by a porous diaphragm of asbestos. An inverted box of slate over the anodes collects the chlorine. The cell body is a steel tank with an outlet for the sodium hydroxide solution. Salt brine flows steadily into the anode compartment. The outflowing solution contains 10 to 12 per cent sodium hydroxide and 14 to 16 per cent of salt, which is precipitated by partial evaporation. This is a simple matter because salt is much less soluble than the hydroxide. The Nelson cell was adopted by our government during the war for chlorine production at the Edgewood arsenal. This cell is guaranteed to produce 60 lb. of chlorine and 65 lb. of sodium hydroxide every 24 hours, using not more than 120 lb. of salt. The cells are rated at 1000 amperes and the voltage drop averages 3.7 volts. At least 2.3 volts are required to secure any decomposition of sodium chloride in water. For more detailed discussion of this new cell read *Jour. Met. & Chem. Eng.*, Vol. 21, 134 (1919).

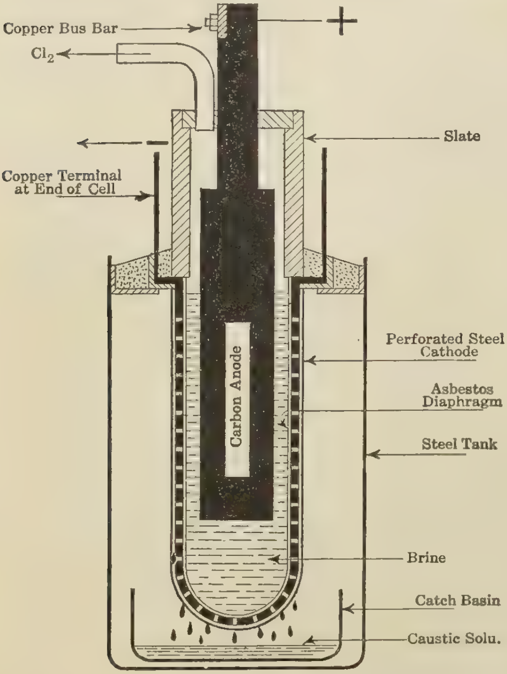


Fig. 94

The hydrogen released at the cathode is sometimes made to unite with the chlorine from the anodes, forming hydrochloric acid. In 1919 the United States produced 347,400 tons of sodium hydroxide. This great tonnage was used in the manufacture of soap, paper, leather, in cleaning, water softening, oil refining, mercerizing cotton, and in making artificial silk by the viscose process. It is the cheapest of the strong bases.

Sodium Carbonate, or Sal Soda, Na_2CO_3. — There are a few natural deposits of "soda," notably the one in British East Africa, where Lake Magadi rests upon thirty square miles of crystallized sodium carbonate. Before 1791 practically all of this salt used was obtained from the ashes of sea plants (inland plants yield potassium carbonate on burning). Naturally sodium carbonate was expensive and, as a result, so was glass and soap. It is scarcely an exaggeration to say that the progress of civilization was greatly retarded for want of a cheap source of sodium carbonate. During the Napoleonic wars France was deprived of its usual supply, so Napoleon offered a prize of 100,000 francs for the discovery of a method for manufacturing an adequate supply from common salt. Le Blanc rose to the occasion.

The Le Blanc Process. — It has been stated that the method was known in England years before 1794, but it must be admitted that Le Blanc made it a commercial success. The materials used are salt, sulfuric acid, coal and limestone. The salt is heated with the concentrated acid to form sodium sulfate with hydrochloric acid as a by-product:

$$(1)\quad 2\,NaCl + H_2SO_4 \rightarrow Na_2SO_4 + 2\,HCl.$$

This is merely the first stage in the process. The sodium sulfate is now mixed with coal and limestone and raked to a hotter part of the furnace. The carbon reduces sodium sulfate to the sulfide, which at once reacts with the limestone forming the desired sodium carbonate:

$$(2)\quad Na_2SO_4 + 2\,C \rightarrow Na_2S + 2\,CO_2,$$

$$(3)\quad Na_2S + CaCO_3 \rightarrow CaS + Na_2CO_3.$$

When the excess coal produces little flames of burning carbon monoxide over the lumps of "black ash" the material is thrown into water to leach out the soda. The insoluble calcium sulfide would tend to make trouble by hydrolysis, yielding soluble CaHS. This would promptly react with the valuable sodium carbonate, precipitating calcium carbonate and ruining everything. Fortunately an excess of lime effectively prevents this hydrolysis. (Write the equation.) In early days the waste calcium sulfide was thrown into streams, where carbon dioxide reacted with it to form hydrogen sulfide, a public nuisance:

$$CaS + H_2CO_3 \rightarrow H_2S + CaCO_3.$$

Driven by law the manufacturers developed the Chance process of sulfur recovery. The above reaction was made use of in the plant and the hydrogen sulfide burned with a limited supply of air. The sulfur set free more than paid the cost of recovery:

$$2\ H_2S + O_2 \rightarrow 2\ H_2O + 2\ S.$$

The Solvay Process. — The Le Blanc method had no rival until 1863 when the Belgians, Ernest and Alfred Solvay, achieved success with their ammonia-soda process. Concentrated sodium chloride solution is saturated with ammonia and carbon dioxide. At first ammonium bicarbonate, $(NH_4)HCO_3$, is formed and this reacts with sodium chloride to form sodium bicarbonate. The latter salt, only sparingly soluble in the salt solution, precipitates and after removal is heated to form sodium carbonate:

$$\begin{aligned}&NH_4OH + H_2CO_3 \rightarrow (NH_4)\ HCO_3,\\&(NH_4)HCO_3 + NaCl \rightarrow NaHCO_3 + NH_4Cl,\\&2\ NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.\end{aligned}$$

The process is carried on in steel towers about 50 feet high and 6 feet wide with numerous shelves and water traps to insure thorough mixing. The gases are led in at the bottom and halfway up the side. The temperature in these carbonating towers should not rise above 35° C.

The economy of operation is great. Instead of wasting the ammonium chloride produced it is heated with lime to release ammonia gas, which, of course, is passed into the towers again. And instead of buying this necessary lime in the open market it is made at the plant by heating limestone to about 900°. The carbon dioxide released from the calcium carbonate is used in the carbonating tower:

$$\begin{aligned}&CaCO_3 \rightarrow CaO + CO_2,\\&Ca(OH)_2 + 2\ NH_4Cl \rightarrow CaCl_2 + 2\ NH_3 + 2\ H_2O.\end{aligned}$$

There is only one thing to mar perfection of economy. The calcium chloride by-product finds a very poor market. The consumption of fuel is much less than in the Le Blanc process and the product is purer.

There is no question of the superior efficiency of the Solvay method and the Le Blanc process would long ago have been discarded but for the value of its by-product, hydrochloric acid. As it is, 95 per cent of the world's soda is Solvay soda. There are only two or three Le Blanc plants in England, a few along the Rhine and none in America. It is probable that the Haber process for making ammonia will be operated in connection with the Solvay process for making soda.

The normal annual production in the United States is about 1,000,000 tons of soda. It is essential to many important industries such as the manufacture of glass, soap, paper, leather, enamels. It is also used in cleansing, water softening, dyeing and oil refining.

Exercise 2. — Draw a sodium carbonate tree, root and branch, like the oxygen tree on page 25.

Sodium carbonate is a white solid, very soluble in water, yielding alkaline solutions by hydrolysis. On concentrating these solutions various hydrates crystallize according to the temperature. Kitner (Zeit. f. Phy. Chem. *39*, 645, 1902) states that below 31.85° the crystals are $Na_2CO_3.10\ H_2O$; above 31.85° and below 35.1°, $Na_2CO_3.7\ H_2O$; and above 35.1° the monohydrate, $Na_2CO_3.H_2O$. The decahydrate is almost 63 per cent water. For long shipments this form would involve high freight costs, so the monohydrate is preferred. On standing in the air the decahydrate effloresces, due to its high vapor tension, and crumbles to a white powder, which is the monohydrate. For some purposes the decahydrate is liked because it dissolves more rapidly. The common names for sodium carbonate are washing soda and sal soda.

Sodium Bicarbonate, $NaHCO_3$. — This so-called baking soda is the direct product of the Solvay process. About one ton out of every seven is sold in that form to be used in baking powders, in medicine, etc. The rest is heated to secure the normal carbonate:

$$2\ NaHCO_3 \rightarrow H_2O + CO_2 + Na_2CO_3.$$

Although Na_2CO_3 solutions are strongly alkaline by hydrolysis, $NaHCO_3$ solutions are neutral to phenolphthalein. Since the latter solutions are perceptibly alkaline to methyl orange, there is really a slight excess of $\overset{-}{OH}$ ions present. But the amount of hydrolysis is small in comparison with that in sodium carbonate solutions. From the formula the student may expect hydrogen ions, but the HCO_3 ion is very stable.

Exercise 3. — Represent by equations the hydrolysis of sodium carbonate.

Baking Powders. — To secure plenty of surface in dough, thus making the product "light," some gas must be released throughout the mixture. Air would do, but it is more convenient to have carbon dioxide released. This can be accomplished by addition of a harmless acid (or acid salt) to baking soda. Lactic acid of sour milk has been used with uncertain results when the amount added was not exactly equivalent to the soda. Cream of tartar baking powders serve the purpose very well. They are mixtures of acid potassium tartrate and sodium bicarbonate. The hydrogen ions from the acid salt unite with the HCO_3 ions from the sodium bicarbonate to form carbonic acid, which breaks down into water and carbon dioxide:

$$\overset{+}{H} + \overset{-}{H}CO_3 \rightarrow H_2CO_3.$$

Phosphate baking powders contain an acid phosphate. Alum baking powders depend upon the acid reaction caused by hydrolysis in alum solutions. With all these the salts left in the food are harmless unless used in excessive quantities.

Sodium Sulfate, Na_2SO_4. — Unlimited quantities of this salt are found in Siberian lakes and great deposits fully 98 per cent pure are located in the southwestern part of the United States. Glauber, the alchemist, used it in medicine as early as the middle of the seventeenth century, hence the name Glauber's salt. It crystallizes below 32.38° as $Na_2SO_4.10H_2O$ and above this transition point as the anhydrous salt, Na_2SO_4. This transition temperature is so definitely marked that it has been used in calibrating thermometers. Considerable quantities are used in glass making. At Stassfurt the magnesium sulfate obtained as a by-product in separating potassium chloride is mixed with a solution of sodium chloride:

$$MgSO_4 + 2\,NaCl \rightarrow MgCl_2 + Na_2SO_4.$$

The sodium sulfate is the least soluble of the four salts and crystallizes out.

Sodium Bisulfate, $NaHSO_4$.— This white, soluble salt is prepared by adding only half enough sodium hydroxide or carbonate to sulfuric acid to neutralize the acid. It is also prepared by addition of sulfuric acid to common salt or to sodium sulfate:

$$NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O,$$

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl,$$

$$Na_2SO_4 + H_2SO_4 \rightarrow 2\,NaHSO_4.$$

The name *acid sodium sulfate* is appropriate, for the salt ionizes as follows:

$$NaHSO_4 \leftrightarrows \overset{+}{Na}+\overset{+}{H}+\overset{--}{SO_4}.$$

On heating the dry salt it is decomposed with formation of water and the pyrosulfate. At higher temperatures this yields sulfur trioxide. Any metallic oxide present is readily converted into sulfate by this sulfur trioxide. A higher temperature can be attained than with sulfuric acid, which boils at 330°:

$$2\ NaHSO_4 \rightarrow H_2O+Na_2S_2O_7,$$
$$Na_2S_2O_7 \rightarrow Na_2SO_4+SO_3.$$

Sodium Sulfite, Na_2SO_3. — The sulfite of sodium is obtained by saturating a solution of the carbonate with sulfur dioxide and then adding an amount of the carbonate just equal to that taken at first:

$$(1)\ \ Na_2CO_3+2\ H_2SO_3 \rightarrow H_2CO_3+2\ NaHSO_3,$$
$$(2)\ \ Na_2CO_3+2\ NaHSO_3 \rightarrow H_2CO_3+2\ Na_2SO_3.$$

It is used in photography and as an *antichlor* in the textile industry. Chlorine left in the fabric after bleaching weakens the fibers, but if sodium sulfite be added the chlorine reacts to form harmless salt. Sulfites readily oxidize in the air, so they are apt to be contaminated with sulfate. They are good reducing agents.

Sodium bisulfite, $NaHSO_3$, is the product of reaction (1). It is used in paper making, chrome tanning, making dyestuffs, and as an antichlor.

Sodium thiosulfate, $Na_2S_2O_3$. — Photographers know this compound as "hypo" and use it to dissolve unused silver bromide from the exposed plates. It is formed very easily by boiling sodium sulfite with sulfur:

$$Na_2SO_3+S \rightarrow Na_2S_2O_3.$$

On acidifying a solution of sodium thiosulfate the acid of which it is a salt is liberated. In other words thiosulfuric acid is set free. This acid is very unstable, breaking down at once into free sulfur and sulfurous acid, which is also unstable:

$$(1)\ \ Na_2S_2O_3+2\ HCl \rightarrow 2\ NaCl+H_2S_2O_3,$$
$$(2)\ \ H_2S_2O_3 \rightarrow H_2SO_3+S,$$
$$(3)\ \ H_2SO_3 \rightarrow H_2O+SO_2.$$

The salt is used in quantitative determination of free iodine because it reacts with iodine to form colorless compounds, sodium iodide and sodium tetrathionate:

$$2\ Na_2S_2O_3 + I_2 \rightarrow 2\ NaI + Na_2S_4O_6.$$

EXERCISE 4. — If a solution of iodine in potassium iodide be added to sodium thiosulfate, what color change takes place? Write the equations.

Sodium Sulfide, Na_2S. — The preparation consists in dividing any solution of sodium hydroxide into two equal parts, saturating one with hydrogen sulfide and mixing the two portions:

$$(1)\quad NaOH + H_2S \rightarrow NaHS + H_2O,$$
$$(2)\quad NaOH + NaHS \rightarrow Na_2S + H_2O.$$

Reduction of sodium sulfate with carbon at 900° also yields sodium sulfide. It is a very soluble crystalline salt. In solution it is strongly basic, due to hydrolysis, since it is a salt of a strong base and a weak acid. It is a necessary aid to the "sulfur colors" in dyeing cotton and is also required in the manufacture of certain dyes. Its solution removes hair from hides and denitrates artificial silk. When a sodium hydroxide solution is heated with sulfur, certain polysulfides of sodium are formed.

Sodium Cyanide, NaCN. — The reduction of sodamide with carbon at red heat produces this salt. The sodamide is prepared by action of ammonia on hot sodium at 300°–400°:

$$2\ Na + 2\ NH_3 \rightarrow 2\ NaNH_2 + H_2,$$
$$NaNH_2 + C \rightarrow NaCN + H_2.$$

The Bucher process of making available the free nitrogen of air will probably lead in production of sodium cyanide (page 169). With iron as a catalyst a reaction takes place between hot soda ash, powdered coal and nitrogen of the air or of producer gas:

$$Na_2CO_3 + 4\ C + N_2 \rightarrow 2\ NaCN + 3\ CO.$$

It is important to produce cheap sodium cyanide because it is much used in extracting gold from low grade ores. A cheap product, good enough for gold extraction, is prepared by heating cyanamide with salt. Prussic acid, HCN, which is released on acidifying the cyanide, is largely used in the fumigation of fruit trees. Cyanides are important in electroplating, case-hardening of steel, and as a fluxing material.

Sodium Nitrate, $NaNO_3$. — This salt has been discussed in previous chapters in connection with nitric acid and fertilizers. The largest deposit is in the dry region of northern Chili, but a few unimportant deposits occur elsewhere. The crude "caliche" is purified by recrystallization from water. It is used somewhat in the cheapest gunpowder, but is too deliquescent for the purpose. Potassium nitrate is preferred.

Sodium Nitrite, $NaNO_2$. — The nitrite is made by heating the nitrate. Loss of oxygen is expedited by heating with lead. The lead oxide formed is separated by filtration from the soluble nitrite:

$$2\ NaNO_3 \rightarrow 2\ NaNO_2 + O_2,$$
$$NaNO_3 + Pb \rightarrow NaNO_2 + PbO.$$

Most of it is produced by passing oxides of nitrogen (from the electric arc) into a solution of sodium hydroxide. The United States uses about 4000 tons of the nitrite annually in the manufacture of dyes.

Exercise 5. — From Chapter XIX learn the method of detecting the difference between a nitrate and a nitrite.

Exercise 6. — What are the reactions involved in the electric arc process of making sodium nitrite?

The Sodium Phosphates. — There are three phosphates of sodium: NaH_2PO_4 of nearly neutral reaction in water; Na_2HPO_4 of faintly basic reaction; and Na_3PO_4 of strongly basic reaction. These are prepared by adding proper amounts of sodium hydroxide to orthophosphoric acid. If the base be added until the solution is neutral to methyl orange, NaH_2PO_4 is formed. It might be expected that such a salt would yield two hydrogen ions per molecule and make the solution very acid. However, the $\overset{-}{H_2PO_4}$ ion is very stable, with only a trifling tendency to ionize further. The reaction is expressed simply enough:

$$NaH_2PO_4 \rightleftarrows \overset{+}{Na} + \overset{-}{H_2PO_4}.$$

Yet it must not be denied that an appreciable, if slight, ionization of $\overset{-}{H_2PO_4}$ does take place:

$$\overset{-}{H_2PO_4} \rightleftarrows \overset{+}{H} + \overset{--}{HPO_4}.$$

This equilibrium is disturbed to the right by the presence of sufficient $\overset{-}{OH}$ ions, so it is possible to add just enough excess of sodium hydroxide to secure the formation of Na_2HPO_4. This is estimated accurately by use of phenolphthalein as indicator, as it does not change color until a greater concentration of $\overset{-}{OH}$ ions is secured than is necessary to change the color of methyl orange. By the same process it may be shown that addition of considerable excess of sodium hydroxide can result in formation of Na_3PO_4. The right proportions are secured by the use of alizarin green as an indicator. A water solution of the trisodium phosphate may have an alkalinity nearly equivalent to 0.1 N sodium hydroxide. The use of this phosphate in washing powders depends on its basic reaction and on its ability to precipitate calcium and magnesium phosphates from hard water. The disodium phosphate is the salt used as a desk reagent. Its presence in the blood is most important in maintaining the right alkalinity.

A detailed discussion of the phosphoric acids and their salts was given in the Phosphorus chapter.

Sodium Peroxide, Na_2O_2. — The simplest oxide of sodium may be obtained by heating the nitrite with sodium in absence of air:

$$2\ NaNO_2 + 6\ Na \rightarrow N_2 + 4\ Na_2O.$$

This oxide reacts violently with water to form sodium hydroxide:

$$Na_2O + H_2O \rightarrow 2\ NaOH.$$

The peroxide is of much greater interest. When sodium in aluminum trays is gradually pushed forward inside hot iron tubes against a counter current of air, a yellow powder is formed. This is the peroxide, a substance widely known as a bleaching agent. It is a source of hydrogen peroxide when acidified. (Equation?) With water it acts vigorously with release of oxygen; consequently it must not be allowed to get wet if in contact with paper, wood or other inflammable material. This ability to release oxygen makes it useful in Parr's method of determining the fuel value of coal:

$$2\ Na_2O_2 + 2\ H_2O \rightarrow 4\ NaOH + O_2.$$

Tests for Sodium Compounds. — There are no insoluble sodium salts except the fluosilicate and the pyroantimonate, $Na_2H_2Sb_2O_7$.

Addition of the soluble potassium pyroantimonate to a solution of a sodium salt yields the latter compound as a precipitate. Sodium salts are recognized by the intense yellow color they give to a colorless flame. The test is too delicate, for even the dust of the air colors a flame yellow. As a rule we report sodium in qualitative analysis only for very intense and prolonged coloration of the flame. With the spectroscope the element is recognized by characteristic yellow lines.

POTASSIUM

Occurrence. — Potassium salts are so essential to soil fertility that the location of workable deposits is of great importance. Feldspar is widely distributed and is responsible by its slow weathering for the available potassium salts in fertile soils. However, the amount removed by continued heavy cropping is not rapidly replaced from this source. As a result the whole civilized world paid tribute to Germany for its possession of the great Stassfurt deposits of the soluble chloride and sulfate of potassium. The Stassfurt mines began commercial production about 1861, after Liebig showed the need of potassium in agriculture.

No doubt an arm of the sea was once cut off by an upheaval of land, and the subsequent evaporation of the brine left this deposit. Naturally there is much sodium chloride present, most of it as the lowest layer, which is half a mile thick. As the brine became more concentrated potassium salts deposited, forming layers not exceeding 100 feet in thickness. Above is a deep layer of sandstone. The minerals dug out at a great profit are sylvite, KCl, and carnallite, $KCl.MgCl_2.6\ H_2O$. Other layers containing magnesium sulfate are of less value. Many millions of tons of these salts have been removed and German authorities claim the deposit will last 1000 years.

During the Great War German scientists boasted that agricultural starvation for want of potassium fertilizers would force the Allies to their knees. Instead, allied scientists developed hitherto neglected sources and now there is a strong probability that industrial countries will become independent in this respect. With Alsace-Lorraine, France secured valuable deposits similar to those at Stassfurt.

The pre-war needs of the United States were for about 200,000 tons, estimated as K_2O, "potash." By diligent extraction of the deposits in lakes in Nebraska, Utah, and California and by other methods we produced about 52,000 tons of potash in 1918. It has also been shown that potash can be extracted from cement mill dust and blast furnace dust. Full utilization of our resources in this respect would furnish more potash than we need. The Utah deposit of alunite, $KAl_3(OH)_6(SO_4)_2$, is readily converted into a soluble potassium fertilizer, as is also the Wyoming leucite. Distance from a larger agricultural market handicaps the development of these mountain deposits. Yet it is stated that in 1920 we secured from 1000 to 5000 tons from each of the following sources: cement mill dust; the two blast furnaces actually working over their dust; beet sugar waste; molasses residues; and Utah alunite. For a time the Wyoming leucite deposit was worked.

The limitless deposits of greensands in New Jersey and adjoining states will probably prove to be one of the chief sources of potassium salts. These greensands, hydrated aluminum potassium silicates, may be heated with lime and water yielding potassium hydroxide directly. Even the abundant feldspar may be made available by the Hopkins process.

Stimulated by war prices a few companies leached potassium salts from the ashes of the giant kelp or seaweed of the California coast. Some iodine and other products were obtained. Present prices have cut down this industry, but its possibilities give us a valuable national asset.

Wood ashes have always furnished a moderate amount of potassium carbonate (the "lye" of colonial days) and small deposits of potassium nitrate are known.

Preparation. — Sir Humphry Davy is usually given credit for being the first to make potassium. In 1807, the same year he made sodium, he electrolyzed moistened potassium hydroxide. Yet it seems more than probable that an American chemist, James Woodhouse of Philadelphia, made the element at about the same time and quite independently of any knowledge of Davy's discovery. Woodhouse died in 1809 and it is certain that some time before his death he made potassium by reduction of "potash" with carbon.

The early American chemists, contemporary with Priestley, deserve far more credit than they received for their discoveries and attainments. Edgar F. Smith, of the University of Pennsylvania, has performed a valuable service in writing the early chemical history of America. He proves that the first chemical society in the world was organized at Philadelphia in 1792. Robert Hare was a genius worthy of lasting fame, and yet the world seemed ignorant until recently of his contributions to science. In 1801 he invented the oxy-hydrogen blowpipe while a lad of twenty. With this device he astounded the great Priestley, then a resident of Pennsylvania, by melting platinum and the most refractory compounds. Later Hare introduced the use of the mercury cathode in electrolysis and by its use prepared calcium amalgam. Greatest of all his achievements was his invention of the electric furnace. He did these things seventy years before modern chemists rediscovered them. Bancroft says, "He was in many respects the precursor of Moissan, although a much more brilliant man than the latter. Hare was born too early."

Woodhouse was a pioneer in the chemistry of the bakery, and explained the rôle played by plants in taking up carbon dioxide from the atmosphere. Both Hare and Woodhouse were native Americans, trained in America. Cooper, Silliman and Cutbush were chemists of great attainments in the early part of the last century. Samuel Guthrie deserves equal credit with Soubeiran, Liebig and Dumas in the discovery of chloroform. He was absolutely the first to put it to medical use.

In justice to such pioneers, American chemists should read Edgar F. Smith's delightful book, *Chemistry in America,* D. Appleton & Co. A short review of this early history is found in *Jour. Ind. Eng. Chem., 11,* 405, 1919.

Potassium may be prepared by electrolysis of the melted hydroxide or chloride, a method applicable to all the alkali metals.

Properties. — Potassium is a silvery white metal, soft, easily tarnishing in air, and reacting violently with water. It is a more active element than sodium, but resembles it in uniting directly with hydrogen, oxygen, the halogens, nitrogen and other elements. Its vapor is blue and its solution in liquefied ammonia is blue.

Potassium Chloride and Other Halides. — The chloride is found nearly pure as sylvite in the Stassfurt deposits. Still more is obtained by cooling a hot, saturated solution of carnallite, $KCl.MgCl_2.6\,H_2O$. The less soluble potassium chloride crystallizes out.

The bromide is prepared by the action of bromine on a solution of potassium hydroxide. On heating, the bromate is converted into bromide:

$$6\,KOH + 3\,Br_2 \rightarrow 3\,H_2O + 5\,KBr + KBrO_3.$$

Exercise 7.—Represent the above reaction by step equations.

Potassium bromide is also made by adding potassium carbonate to the solution obtained by mixing bromine and iron. Compare with the methods of making sodium bromide. The iodide is prepared by methods similar to those used for sodium iodide. Both potassium bromide and iodide are used in photography and medicine.

Potassium Hydroxide. — This strong base does not differ much from sodium hydroxide in properties, preparation, or uses. Besides the electrolytic method it has been made by boiling together lime and potassium carbonate solution. The calcium carbonate is removed by filtration:

$$Ca(OH)_2 + K_2CO_3 \rightarrow CaCO_3 + 2\ KOH.$$

The chief use for potassium hydroxide is in the manufacture of soft and liquid soaps. For other purposes the cheaper sodium hydroxide serves as well.

Potassium Carbonate, K_2CO_3. — This salt, like the very similar sodium carbonate, can be made by the Le Blanc process. It was formerly leached from wood ashes. Some was secured by igniting wool fat. However, most of it is prepared from magnesium carbonate and potassium chloride:

$$2\ KCl + 3\ MgCO_3 + H_2O + CO_2 \rightarrow MgCl_2 + 2\ MgKH(CO_3)_2.$$

On heating the last named salt more magnesium carbonate is produced with more carbon dioxide, both needed in the above reaction:

$$2\ MgKH(CO_3)_2 \rightarrow 2\ MgCO_3 + H_2O + CO_2 + K_2CO_3.$$

The leading use for potassium carbonate is in making hard glass.

Potassium Chlorate, $KClO_3$. — The methods of preparation from chlorine and potassium hydroxide or in the electrolysis of potassium chloride have been given in Chapter IX. Its use in the preparation of oxygen and as a solid oxidizing agent in matches, fireworks, and explosives was also mentioned.

Potassium bromate and iodate need no further comment. They are similar to the chlorate.

Exercise 8. — Assume that 100 g. of water is saturated with both sodium nitrate and potassium chloride at 40°. If 50 g. of water be evaporated while holding the temperature at 60°, what weight of each salt must crystallize out at 60°? On cooling to 0° what weight would crystallize out? Consult the solubility curves on page 90.

Potassium Nitrate, KNO_3. — Potassium nitrate has long been used in gunpowder. It was formerly obtained in small deposits in Bengal, hence the name, Bengal saltpeter. Scheele discovered oxygen by heating this salt. It is now prepared by mixing saturated solutions of sodium nitrate and potassium chloride. On cooling, the less soluble potassium nitrate crystallizes out:

$$KCl + NaNO_3 \leftrightarrows NaCl + KNO_3.$$

It forms rhombic crystals melting at 345°. Some of it is used in medicine, some to preserve meat, which it colors red, but most of it is still used in black gunpowder. This explosive is essentially 75 parts potassium nitrate, 10 parts sulfur, 14 parts charcoal and 1 part water. It is mixed and ground wet and then dried carefully. On explosion, expanding gases form. The smoke is due to solid potassium sulfide:

$$2\ KNO_3 + 3\ C + S \rightarrow N_2 + 3\ CO_2 + K_2S.$$

Potassium Cyanide, KCN. — This compound is similar in every way to sodium cyanide. It has usually been prepared by heating potassium ferrocyanide, $K_4Fe(CN)_6$, which itself was made by heating animal refuse (as a source of nitrogen) with scrap iron and potassium carbonate:

$$K_4Fe(CN)_6 \rightarrow 4\ KCN + FeC_2 + N_2.$$

Since the product is largely used in extracting gold from low grade ores, the yield is often increased by addition of sodium to the ferrocyanide. The mixed cyanides are effective in metallurgy:

$$K_4Fe(CN)_6 + 2\ Na \rightarrow 4\ KCN + 2\ NaCN + Fe.$$

It is also possible to prepare potassium cyanide by passing ammonia over a mixture of carbon and fused potassium carbonate.

Potassium Sulfate, K_2SO_4. — Some potassium sulfate occurs in the Stassfurt mineral known as schonite, $K_2SO_4.MgSO_4$. It is separated by addition of potassium chloride. On concentrating the potassium sulfate crystallizes first:

$$K_2SO_4.MgSO_4 + 2\ KCl \rightarrow MgCl_2 + 2\ K_2SO_4.$$

It is also a product of the action of sulfuric acid on potassium chloride under proper conditions:

$$H_2SO_4 + 2\ KCl \rightarrow 2\ HCl + K_2SO_4.$$

This sulfate is mixed with aluminum sulfate to make alum. It is also used as a fertilizer. The acid sulfate or potassium bisulfate is prepared by mixing sulfuric acid and potassium chloride in the right proportions and at a lower temperature than is required for the normal sulfate:

$$H_2SO_4+KCl \rightarrow HCl+KHSO_4.$$

On being heated to a sufficient temperature it loses water (like sodium bisulfate) and forms the pyrosulfate, $K_2S_2O_7$. At higher temperatures a loss of sulfur trioxide occurs. Consequently this, like the similar sodium salt, is useful in transforming certain insoluble minerals into sulfates.

Potassium Sulfide, K_2S. — There is no particular interest in this salt. In preparation and properties it simply parallels the sodium salt.

Tests for Potassium Compounds. — The potassium flame is violet, but is easily masked by the intense yellow of the sodium flame. It is well to view the flame through a thick blue glass, which cuts off the yellow light.

The potassium ion unites with the chloroplatinate ion to form insoluble potassium chloroplatinate, K_2PtCl_6:

$$H_2PtCl_6+2\ KCl \rightarrow 2\ HCl+K_2PtCl_6.$$

The precipitate is composed of yellow octahedra. The solution of potassium salt must be rather concentrated and precipitation is aided by addition of a little alcohol. This reaction is the basis of a standard method of determining potassium quantitatively. Due to the great expense of the chloroplatinic acid the perchlorate method is coming into use. Perchloric acid is added to a solution of a potassium salt. White potassium perchlorate, $KClO_4$, is precipitated, particularly in the presence of alcohol.

Addition of a solution of sodium cobaltinitrite, $Na_3CO(NO_2)_6$, to a neutral or faintly acid solution of a potassium salt yields a yellow precipitate of potassium cobaltinitrite, the least soluble of all potassium salts.

Other comparatively insoluble potassium salts of interest in recognition of potassium ion are the picrate, $C_6H_2(NO_2)_3OK$, the hydrofluosilicate, K_2SiF_6, and the acid tartrate, $KHC_4H_4O_6$.

AMMONIUM

Ammonia gas, NH_3, has been discussed and we are familiar with the fact that it unites directly with hydrogen chloride to form a salt, ammonium chloride:

$$NH_3 + HCl \rightarrow NH_4Cl.$$

The existence of this and other salts containing the ammonium radical, NH_4, makes it necessary to class this radical with the alkali metals. It is true the radical has never been isolated, but in its compounds it strongly resembles sodium and potassium.

The nearest we have come to isolating this "hypothetical metal" is in the preparation of *ammonium amalgam*. On electrolyzing a concentrated solution of an ammonium salt with a mercury cathode, the ammonium ion $\overset{+}{NH_4}$ is discharged on the mercury in which the metal dissolves or amalgamates. Mercury never dissolves anything but a metal. Addition of a dilute sodium amalgam to a cold concentrated solution of ammonium chloride also yields ammonium amalgam:

$$NH_4Cl + Na(Hg) \rightarrow NaCl + NH_4(Hg).$$

On allowing the solution to become warm the amalgam becomes astonishingly voluminous, due to the formation of ammonia and hydrogen. Finally only mercury and salt are left in the water. Evidently the ammonium displaces hydrogen from water just as sodium does:

$$2\ NH_4(Hg) + 2\ H_2O \rightarrow 2\ Hg + H_2 + 2\ NH_4OH,$$
$$NH_4OH \rightarrow NH_3 + H_2O.$$

Ammonium Hydroxide, NH_4OH. — This base is formed by union of ammonia gas with water:

$$NH_3 + H_2O \leftrightarrows NH_4OH.$$

It seems probable that in a 0.1 N solution, for example, most of the ammonia is merely in solution as NH_3 and only a little of it in the combined form of NH_4OH. Ammonium hydroxide is ranked as a weak base and it may be weak, but it is also possible that the small amount of actual ammonium hydroxide present may ionize very well. At −79° this base is a solid. The oxide has never been prepared.

Ammonium Chloride, NH_4Cl. — This salt crystallizes in cubes or octahedra. At 350° it dissociates into ammonia and hydrogen chloride. On cooling the gases unite to form a smoke of ammonium chloride. The equilibrium is displaced by change in temperature:

$$NH_4Cl \leftrightarrows NH_3+HCl.$$

Of course if heated in an atmosphere of either ammonia or hydrogen chloride the equilibrium would be displaced to the left. Better "opportunity for contact" between the two gases accounts for this. "Mass action" is another phrase for the same thing. The salt is made by passing ammonia into hydrochloric acid or by heating together ammonium sulfate and sodium chloride. Its use in soldering depends on its ability to clean off oxides, allowing metallic surfaces to be brought into contact. Its largest use is in the manufacture of over 50,000,000 dry cells each year in the United States alone.

Ammonium Sulfate, $(NH_4)_2SO_4$. — The sulfate is a product of coal gas works. Ammonia is passed directly into sulfuric acid, forming this salt. It is the source of many other ammonium compounds. As a source of nitrogen in fertilizers it is needed to the extent of half a million tons in this country alone. Germany uses nearly as much.

Ammonium Nitrate, NH_4NO_3. — There are three transition points of this salt, at 35°, 83° and 126°. It melts at 160° and at higher temperatures decomposes into water and nitrous oxide:

$$NH_4NO_3 \rightarrow H_2O+N_2O.$$

Most ammonium salts on heating yield ammonia, but this is an exception. It explodes if heated too rapidly. In the recent war it was mixed with T. N. T. and other high explosives, adding greatly to military resources. There wasn't enough T. N. T. while ammonium nitrate was cheap and made in unlimited quantities. Once started it explodes with terrific force.

Ammonium Nitrite, NH_4NO_2. — The unstable nitrite must be prepared as needed by mixing solutions of any ammonium salt with any nitrite. On gently warming the mixture nitrogen is evolved:

$$NaNO_2+NH_4Cl \leftrightarrows NaCl+NH_4NO_2,$$
$$NH_4NO_2 \rightarrow 2\,H_2O+N_2.$$

Ammonium Carbonate, $(NH_4)_2CO_3$. — Saturation of ammonium hydroxide with carbon dioxide produces ammonium bicarbonate,

$(NH_4)HCO_3$. This decomposes easily on heating, yielding ammonia, carbon dioxide and water, hence its use as a sort of baking powder. Addition of excess ammonium hydroxide to this salt forms normal carbonate which is rather unstable. The commercial product is a mixture of the bicarbonate and ammonium carbamate, $NH_4CO_2NH_2$. To prepare it powdered calcium carbonate is mixed with ammonium sulfate and sublimed.

Ammonium Sulfide, $(NH_4)_2S$. — When ammonia and hydrogen sulfide gases are mixed in proper proportions the normal sulfide, $(NH_4)_2S$, or the acid sulfide, $(NH_4)HS$, may be formed. Saturation of a solution of ammonium hydroxide with hydrogen sulfide yields the soluble ammonium hydrosulfide. Addition of excess ammonium hydroxide to this solution yields the normal sulfide:

$$(1)\ NH_4OH + H_2S \leftrightarrows (NH_4)HS + H_2O,$$
$$(2)\ (NH_4)HS + NH_4OH \leftrightarrows H_2O + (NH_4)_2S.$$

The normal sulfide, which is colorless, is rather unstable because of hydrolysis, as indicated by the reversibility of reaction (2). It is much used in qualitative analysis to precipitate certain sulfides. Excess ammonium hydroxide helps to retard this hydrolysis. On standing, especially in the light, the air oxidizes the hydrogen sulfide released. The sulfur formed unites directly with the ammonium sulfide to form such yellow or red polysulfides as $(NH_4)_2S_2$, $(NH_4)_2S_3$ and $(NH_4)_2S_5$. This solution of "yellow" ammonium sulfide is used in analysis to dissolve the sulfides of arsenic, antimony and tin.

Tests for Ammonium Salts. — These salts are isomorphous with potassium salts and form similar precipitates. However, they may be distinguished without great difficulty. All ammonium salts on warming with a base give off ammonia gas, recognized by odor and by its ability to turn moist red litmus paper blue:

$$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2\ NH_4OH,$$
$$NH_4OH \leftrightarrows NH_3 + H_2O.$$

RUBIDIUM AND CÆSIUM

Bunsen and Kirchoff, in 1860, working with the spectroscope which they had just invented, discovered certain peculiar bright lines in the spectrum of the residue from a spring water. This clue led them to the discovery of the elements, rubidium and cæsium, responsible for the lines. Rubidium (*rubidius*, dark red) received its name from two very bright red lines, and cæsium (*cæsius*, sky-blue) from two bright blue lines. Compounds of these elements are found in very small amounts in carnallite and in lepidolite. There is a small deposit of the mineral *pollux* containing 34 per cent cæsium (estimated as the oxide).

The elements are of no practical interest. In a general way their chemistry is much like that of the rest of the alkalies. They are the most active elements of the group, taking fire at ordinary temperatures when exposed to dry oxygen.

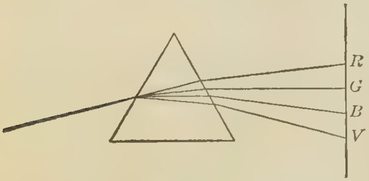


FIG. 95

The Spectroscope. — A beam of sunlight passing through a transparent prism is dispersed into the colors composing white light (Fig. 95). This is due to the fact that in entering one transparent medium from another the different wave lengths of light are bent in different degrees. Against a white screen these colors are projected in a band called the spectrum. The spectroscope (Fig. 96) consists of a glass prism, a tube containing lenses and an adjustable slit to admit a narrow beam of light, a telescope with which to view the spectrum, and a third tube which projects the image of a measuring scale on the field. Small direct vision spec-

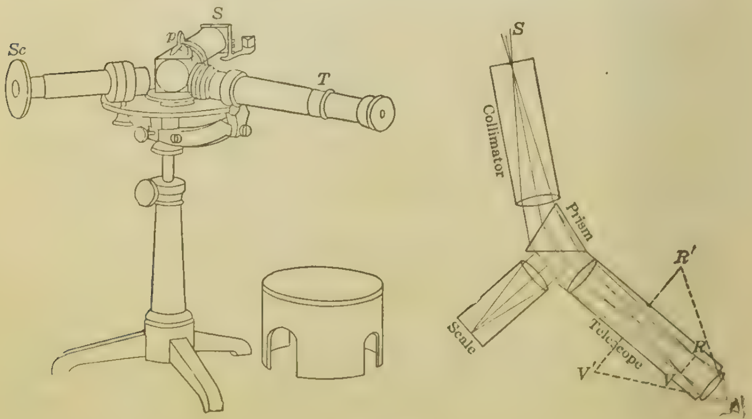
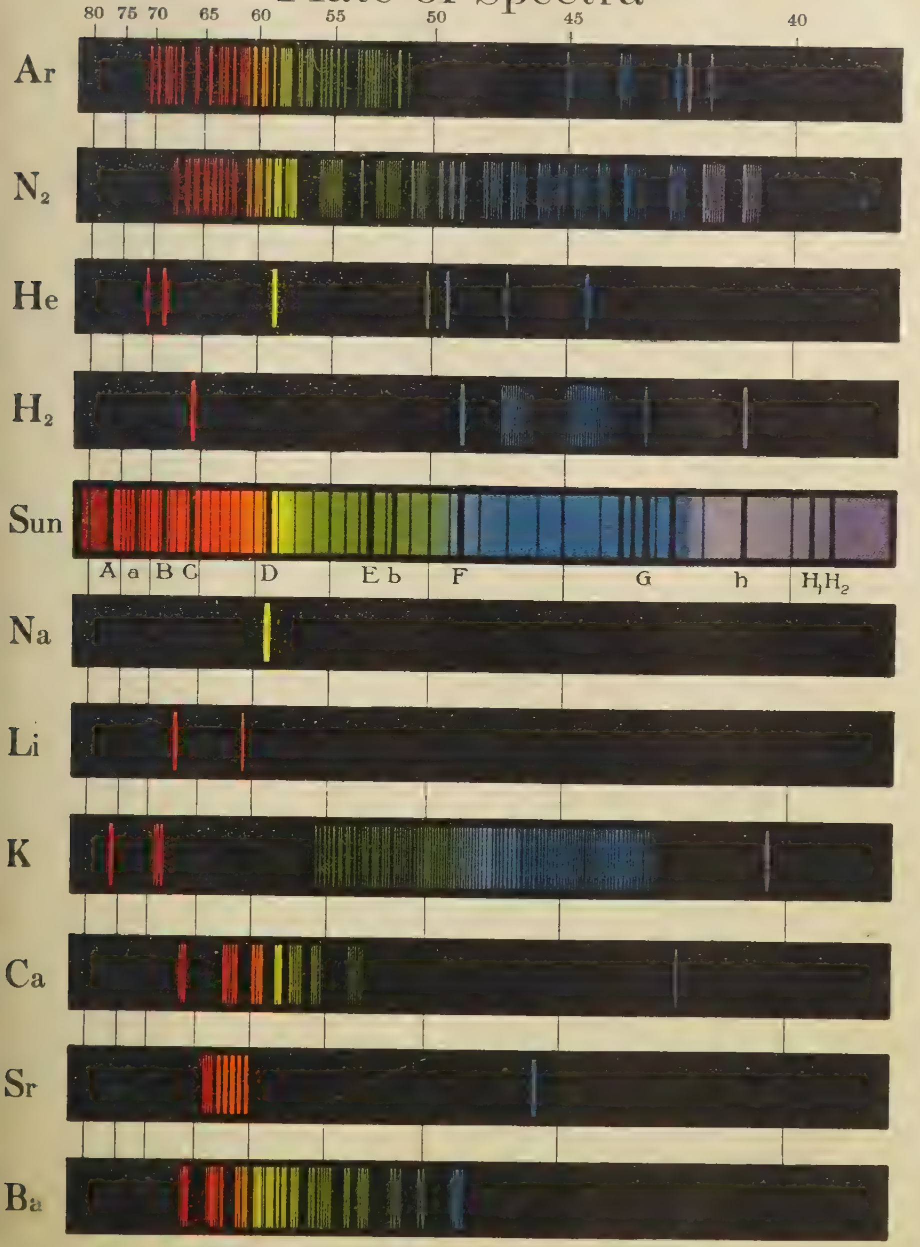


FIG. 96

Plate of Spectra



From *Inorganic Chemistry*, by H. P. Cady.
By permission of the author and McGraw-Hill Book Co., Publishers.

troscopes are made of a single tube with lens, prism and slit inside the tube.

Wave lengths shorter than the visible are called "ultraviolet" and have considerable actinic power. They are the cause of sunstroke and probably convert some of the oxygen of the upper atmosphere into ozone. Heat waves are longer than the visible wave lengths.

Bright-line Spectra. — An incandescent solid gives a continuous spectrum of all wave lengths. An incandescent gas gives a spectrum made up of one or more bright lines, sometimes a large number. These are always characteristic of each element, both in color and in the exact position of the lines. For example, if light from a sodium flame be viewed through the spectroscope a single yellow line is observed. Incandescent helium gives a spectrum of definitely located red, yellow, green and blue lines, and may be recognized by them.

Dark-line Spectra. — The spectrum of the incandescent sun is really not continuous but contains many dark lines (Frauenhofer lines, because they were first mapped by Frauenhofer in 1814). These are explained by the fact that when, for example, light from a white-hot solid passes through a yellow sodium flame there is a dark line in the yellow part of the spectrum. In other words, a gas which, when incandescent, is capable of producing certain definite lines in the spectrum absorbs those very lines from light passed through the gas. It is evident, then, that the gaseous envelope around the sun absorbs certain wave lengths of light and gives us a dark-line solar spectrum instead of a continuous one. Due to this fact we learned of the existence of helium in the sun's atmosphere thirty years before it was found on earth. Included in the solar gases are the terrestrial elements, sodium, calcium, iron, hydrogen, manganese, carbon, silver, and others to the number of forty or more.

Liquids absorb certain wave lengths, giving a dark-band spectrum. Without question the spectroscope is a delicate and invaluable analytical tool.

CHAPTER XXVIII

THE ALKALINE EARTH METALS

Element		Atomic Weight	Density	Melting Point	Specific Heat
Calcium	(Ca)	40.1	1.55	810°	0.152
Strontium	(Sr)	87.63	2.54	900°	—
Barium	(Ba)	137.37	3.75	850°	0.068

To this list should be added radium, but due to its peculiar relation to uranium it will be discussed in connection with that element. The metals of this group are like the alkalies in that they form rather strong bases. A fancied resemblance to the "earthy" (earth-like) oxides of iron and aluminum led to the old name, "alkaline earths."

All the elements are bivalent in their compounds. All are active, displacing hydrogen from cold water with moderate speed. They are silvery white metals when freshly cut, but quickly tarnish in air due to formation of the oxides and probably the carbonates. They are somewhat harder than lead.

All are made by electrolysis of their melted hydroxides or chlorides, but none have, as yet, any commercial use. Calcium hydroxide is slightly soluble (lime water) and strontium hydroxide and barium hydroxide somewhat more so. The sulfate of barium is extremely insoluble (1:400,000), of strontium rather insoluble (1:8,000), while calcium sulfate is slightly soluble (1:500). All the carbonates are insoluble, while the bicarbonates are soluble.

Calcium

Occurrence. — Calcium compounds are very common in the earth's crust. The most important is the carbonate, $CaCO_3$. Gypsum, $CaSO_4.2\,H_2O$, is very plentiful. The world has only a few great deposits of the fossil rock, phosphorite, $Ca_3(PO_4)_2$, and the best of them are in the United States. Other calcium minerals are apatite, $3\,Ca_3(PO_4)_2.CaF_2$ or $3\,Ca_3(PO_4)_2.CaCl_2$, fluorspar, CaF_2, and dolomite which is a mixture of the carbonates of calcium and magnesium. The solid matter of bones is largely calcium phosphate.

Preparation. — In 1808 Davy prepared the three alkaline earth metals by electrolysis of their fused hydroxides. Calcium is now made by electrolysis of the melted chloride in a carbon or iron cell. The metal is molten when liberated and floats to the top of the bath,where it is chilled and slowly lifted out as a growing stick. In one process this solid stick of calcium forms the cathode.

Properties. — Calcium is a silver-white metal, melting at 800°. Its density is 1.55. The metal can be rolled and drawn. When hot it can be worked much more easily, but oxidation increases rapidly with rise in temperature. The hot metal unites readily with both oxygen and nitrogen; hence it can be used in securing a vacuum. Its nitride yields ammonia in contact with water:

$$Ca_3N_2+6\,H_2O \rightarrow 3\,Ca(OH)_2+2\,NH_3.$$

With hydrogen the hot metal forms a solid hydride known commercially as *hydrolite*. This is a convenient, portable source of hydrogen for military purposes:

$$CaH_2+2\,H_2O \rightarrow Ca(OH)_2+2\,H_2.$$

Since calcium is very active, it also unites directly, when hot, with the halogens, sulfur and phosphorus. It is possible that calcium might be used as a deoxidizer of molten metals if it were cheaper.

Calcium Carbonate. — Vast beds of limestone are found in most countries. Other forms of the carbonate are marble (composed of small calcite crystals) and chalk. Marl is a mixture of limestone and clay. Chalk is made up of the skeletons of minute marine organisms. Sea-shells, corals, pearls, and egg shell are familiar forms of calcium carbonate.

Pure crystallized calcium carbonate is found in two forms, aragonite and calcite, differing in crystal shape and density. When the carbonate is formed in solutions above 30° aragonite crystals deposit, but below 30° calcite crystals are obtained.

Calcium carbonate is practically insoluble in water, as one liter holds only 13 mg. of the salt. But when water is saturated with carbon dioxide the solubility of the carbonate increases thirty fold. To be exact, the bicarbonate is formed:

$$CaCO_3+H_2CO_3 \rightarrow 2\ Ca(HCO_3)_2.$$

Rain washes the carbon dioxide of the air into the soil and as this carbonated water trickles over beds of limestone the soluble bicarbonate forms and the rain water becomes "hard." In many places underground caves are formed in this manner. Some springs deposit this dissolved rock when the sudden decrease of pressure on the water allows the escape of carbon dioxide. Travertine, the rock used in building ancient Rome, was formed in this way. Marble is familiar as an ornamental building material.

Limestone has many uses. As a source of lime it is mined in great quantities. Cement, glass and ceramic material require much more. Modern agriculture approves the use of ground limestone as well as lime in correcting the acidity of soils. Calcium carbide and cyanamide both require limestone or lime as a raw material.

Calcium Oxide, CaO. — This oxide, known as quicklime, is usually obtained by heating limestone:

$$CaCO_3 \leftrightarrows CaO+CO_2.$$

At ordinary temperatures the vapor tension of carbon dioxide from limestone or any similar carbonate is too small to measure. But at elevated temperatures this pressure becomes more than appreciable. Measurements are quoted from W. A. Noyes:

600°	700°	800°	898°	950°
2.35 mm.	25.3 mm.	168 mm.	760 mm.	1490 mm.

In a sealed tube the reaction is reversible, but if a good draught of air carries away the carbon dioxide, thus reducing its partial pressure, the limestone may be completely decomposed below 750°. A current of steam has the same effect. As a rule lime-kilns operate at temperatures of 750°-900°. Of course if the lime were allowed to cool in an atmosphere of carbon dioxide the carbonate would be formed again, since it is a reversible reaction, but this is not done.

The ancient method of burning limestone was to pile up a heap of the carbonate in large lumps over some wood, finally building an arched dome of large fragments over the heap and covering all with dirt. With proper control of the draught the heat of the burning wood or coal was enough to decompose the limestone. In recent years limekilns have been built of fire brick towers and charged from the top with alternate layers of limestone and fuel. The lime, mixed with ashes, was drawn out from the bottom. Obviously such lime could not be used when whiteness is desirable.

The modern kiln is heated by indirect firing (Fig. 97). Two furnaces are built against the sides of the tower and the flames from wood, coal or oil are led into the tower without introduction of ash. Wood is better than coal because the flame is longer. Also the moisture in the wood helps to sweep out the carbon dioxide, thus aiding decomposition of the carbonate. Sometimes a jet of steam is introduced for the same purpose. The gas-fired kiln is best and to-day there are groups of six towers arranged around one gas producer. Some towers are 60 ft. high and 7 feet wide, inside. Such kilns are continuous in operation, producing over 25 tons of lime daily for each tower. With producer gas as the fuel one ton of coal burns 5 or 6 tons of lime. Still wider kilns producing 60 tons daily have been built.

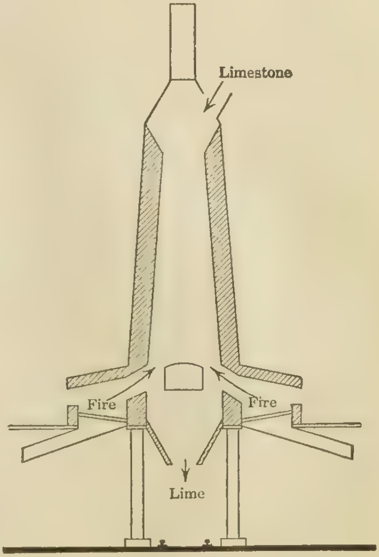


Fig. 97

If the temperature exceeds 1200° the surface of some lumps fuses, due to impurities. When such lime is used on finished surfaces, these lumps may be slow to slake. Later they expand and cause blistering.

Calcium oxide is a white solid melting at about 2750° and boiling at higher temperatures. Heated by the oxyhydrogen flame it becomes brilliantly incandescent and was once used as a source of light for lantern projection (the "lime light"). In the electric arc the oxide vaporizes. On condensing, these vapors form crystals. Calcium oxide is very difficult to reduce. Potassium and sodium are able to reduce it only at the temperature of the electric furnace.

Pure calcium oxide takes up 31.1 per cent of its own weight of water, but the usual impurities lessen this amount. As the oxide hydrates to form the hydroxides much heat is evolved. In fact quicklime stored in wood has often caused fires by accidental reaction with water. Considerable increase in volume also takes place on slaking. The water is first absorbed and then reacts:

$$CaO+H_2O \rightarrow Ca(OH)_2.$$

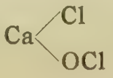
On long exposure to the air quicklime becomes "air slaked," changing into the hydroxide and the carbonate.

In 1910 the United States used 3,481,780 tons of lime for water softening, sugar clarifying, and the manufacture of mortar, plaster, bleaching powder, sprays, paper, leather, and sand-lime bricks. Some gases are dried over lime. Some uses named for limestone apply to quicklime. In agriculture, soil acidity is neutralized by either lime or limestone. However, too much quicklime causes an actual loss of soil nitrogen in the form of ammonia to the air. Ground limestone can do no harm.

Calcium Hydroxide, $Ca(OH)_2$. — Slaked lime is a white powder formed by careful addition of water to quicklime. It is slightly soluble, 100 cc. of water dissolving 0.17 g. at 18°. At higher temperatures it is less soluble. The little that is in solution ionizes rather well, but when considerable quantities of a base are required it is customary to use a suspension of the solid in water known as "milk of lime." As fast as the little in solution is used up some of the suspended hydroxide goes into solution:

$$\underset{\text{undissolved}}{Ca(OH)_2} \leftrightarrows \underset{\text{dissolved}}{Ca(OH)_2} \leftrightarrows \underset{\text{ionized}}{\overset{++}{Ca}+\overset{-}{OH}+\overset{-}{OH}}.$$

This is the cheapest base known and has many industrial uses. In making mortar, plaster, alkalies, bleaching powder, purifying illuminating gas, removing hair from hides and clarifying sugar solutions it is important. Naturally some of these uses duplicate those for the oxide.

Bleaching Powder,  $Ca\begin{cases}Cl\\OCl\end{cases}$. — A full discussion of this "chlorine carrier" was given on page 129 and need not be repeated. By the most modern (and humane) process of manufacture a traveling belt carries slaked lime down a long tunnel against a stream of chlorine gas. This is the principle of counter currents now so well known. The full strength of chlorine gas first meets the powder that is nearly completely chlorinated. Bleaching powder should contain about 35 per cent available chlorine. It is being supplanted for water treatment by liquid chlorine.

Exercise 1. — Prove that bleaching powder is not a mixture of $CaCl_2$ and $Ca(ClO)_2$.

Exercise 2. — What is the effect of moist carbon dioxide on bleaching powder?

Exercise 3. — Is bleaching powder hydrolyzed?

Mortar. — Mortar, to the bricklayer, is a mixture of slaked lime, sand and water which hardens slowly by drying. The chemist knows that carbon dioxide of the air penetrates the wet mortar and reacts with the calcium hydroxide to form solid interlacing crystals of calcium carbonate, $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$. The sand, preferably with sharp edges, merely gives bulk, rigidity, increases porosity and reduces shrinkage. Yet even the chemist is surprised to learn that some mortar in Roman walls 2000 years old has not been completely carbonated. Evidently mere drying does account for much of the solidity of mortar. Possibly the colloidal particles of calcium hydroxide "set" in some way suggestive of the drying of glue or water glass. Wall plaster differs from mortar only in containing hair as a binder. It is porous enough to allow considerable circulation of air through the walls.

Calcium Sulfate, $CaSO_4$. — The dihydrate of this salt, $CaSO_4$-$2\,H_2O$, is found as gypsum in Michigan, Ohio, New York, Virginia, Kansas, Oklahoma and other states. It is heated just enough to cause the loss of three fourths of its water, leaving the hemihydrate, $2\,CaSO_4.H_2O$, or plaster of Paris. This residue, when mixed with the proper amount of water, sets to a white solid in from 5 to 15 minutes. What really happens is a reaction producing interlacing crystals of the dihydrate. The white finishing coat of common plastered walls is plaster of Paris. Statuary is often made from it, because the material expands slightly on setting, thus taking a very sharp impression of the mold. For commercial work such as white plaster, stucco and interior wall bricks, the setting process is retarded by glue or a product made by digesting hair with sodium hydroxide. The anhydrous salt is used in making Keene cement, as a hard finish plaster, and as a filler for glazed paper. The United States uses over 2,000,000 tons of gypsum annually, most of it for plaster. Blackboard crayons are made of a mixture of the hydrated calcium sulfate with some ordinary plaster of Paris, which is mixed with water and allowed to set. The product is sufficiently soft for use. Plaster casts used by the surgeon are made of common plaster of Paris.

Calcium Chloride, $CaCl_2$.—The mineral tachydrite, $CaCl_2 \cdot MgCl_2 \cdot 12\ H_2O$, occurs in the Stassfurt salt layers. Some calcium chloride is found in salt brines and is removed from the bitter liquors. Most of the supply, however, is obtained as a by-product in the ammonia soda process. The hexahydrate, $CaCl_2 \cdot 6\ H_2O$, crystallizes from very concentrated solutions at ordinary temperatures. When heated to 200° it loses some water, leaving a porous, white mass of $CaCl_2 \cdot 2\ H_2O$. This hydrate is very deliquescent and is a good dryer. Heated to 260° the last of the water escapes, leaving the anhydrous salt. This form of the chloride melts at 800°. On evaporating at elevated temperature hydrolysis is increased and some oxide or basic chloride forms. A remarkable freezing mixture is secured by addition of the hexahydrate to a little less than its own weight of snow or ice shavings. By this means a temperature of $-55°$ may be secured. The anhydrous salt is not suitable because its heat of solution is large.

As a drying agent calcium chloride has its limitations. Ammonia cannot be dried over it because of the formation of $CaCl_2 \cdot 8\ NH_3$. For a similar reason it is not suitable for the dehydration of alcohol. Concentrated sulfuric acid is a better dryer and phosphorous pentoxide the most powerful of all. Even $CaCl_2 \cdot H_2O$ has an appreciable vapor tension and so its action is a trifle short of perfect drying. More of this salt is produced commercially than is needed. It finds a limited market as a dust layer, in antifreeze solutions, in coal washing, in tempering metals and chiefly in forming a refrigerating brine for ice plants and cold storage buildings.

Calcium Fluoride, CaF_2. — This salt occurs in nature as the mineral fluorspar. It melts at 1330° and is in demand as a slag former in metallurgy. Addition of calcium fluoride to some other salts lowers the melting point of the mixture. Opaque glass and enamels are often made, with addition of fluorspar. As a source of hydrofluoric acid it is already familiar to the student.

Calcium Sulfide, CaS. — Like all sulfates calcium sulfate is reduced to the sulfide on being heated with carbon:

$$CaSO_4 + 2\ C \rightarrow CaS + 2\ CO_2.$$

It is almost insoluble but is slowly hydrolyzed to the somewhat soluble hydrosulfide, $Ca(HS)_2$. It has some little use as a depilatory and in making luminous paint. Like barium sulfide it gives off light after exposure to bright light. The pure sulfides do not possess this property, but are excited by traces of vanadium and bismuth compounds.

EXERCISE 4. — What relation has calcium sulfide to the Le Blanc soda process?

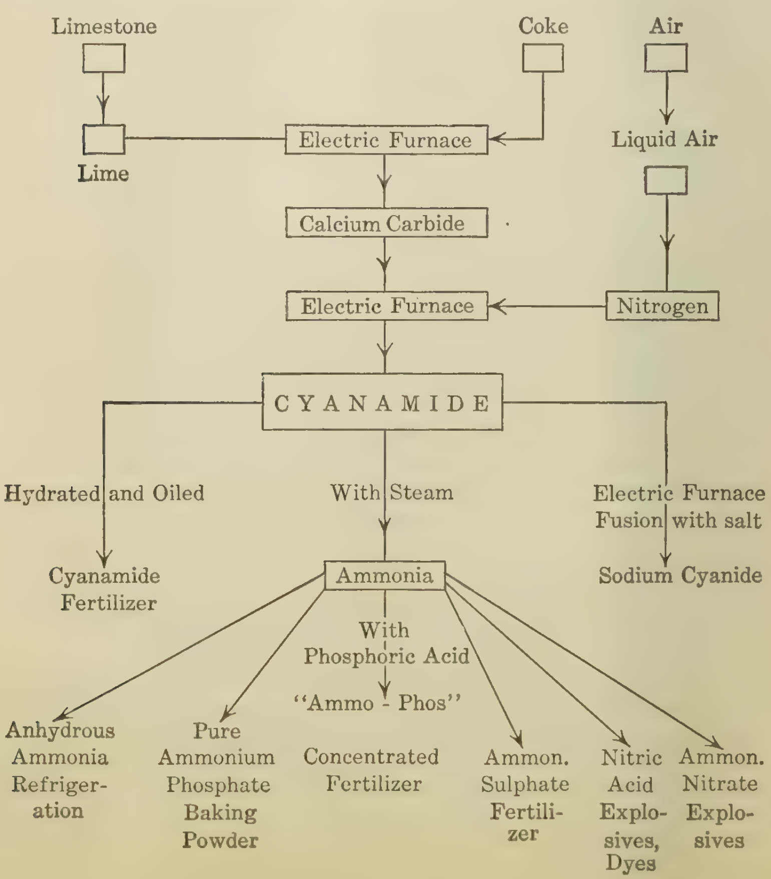
Calcium Phosphate, $Ca_3(PO_4)_2$. — The greater part of the weight of bones and teeth is due to calcium phosphate, so it is no surprise to learn of enormous beds of this salt left as the fossil remains of extinct organisms. The best of these deposits are in Florida, Tennessee and South Carolina, although France controls extensive deposits in northern Africa. Recent investigations indicate that an almost unlimited bed of this material occurs in Montana, Wyoming and Idaho. Since phosphates are a necessity in agriculture, a country like ours possessing most of the known supplies is most fortunate to say the least. The normal phosphate is insoluble and must be converted into the soluble monocalcium salt, $Ca(H_2PO_4)_2$, by reaction with some acid. The commercial practice is to treat ground rock with sulfuric acid in the proportions indicated in the following equation:

$$Ca_3(PO_4)_2 + 2\ H_2SO_4 + 4\ H_2O \rightarrow 2\ CaSO_4.2\ H_2O + Ca(H_2PO_4)_2.$$

The solid mixture of gypsum and monophosphate is sold as "superphosphate of lime." It is now evident that ground phosphate rock itself can be utilized by plants if it be plowed under with a green forage crop. Weak organic acids developed by fermentation of the green crop slowly convert the rock into the soluble monocalcium phosphate. In 1910 the United States produced 2,655,000 tons of phosphate and exported 1,100,000 tons.

Apatite, $3\,Ca_3(PO_4)_2.CaCl_2$, is found in Canada, Norway and Spain.

Other Compounds of Calcium. — Calcium nitrate, $Ca(NO_3)_2$, is a by-product of the arc process of making nitric acid. It is the base of a good fertilizer. ***Calcium carbide, CaC_2,*** discussed on page 225, has been useful as a source of acetylene and as the starting point in the manufacture of cyanamide. Now it gives promise of becoming the starting point in the manufacture of alcohol, acetic acid, acetone and other important organic chemicals. It was first made by E. Davy in 1836, but it was not until 1893 that its manufacture was made commercially successful by the Canadian, Willson.



Cyanamide, $CaCN_2$. — Cyanamide (see page 225) is formed by passing nitrogen over calcium carbide at 1000°:

$$CaC_2+N_2 \rightarrow CaCN_2+C.$$

Steam decomposes it into ammonia and calcium carbonate:

$$CaCN_2+3\ H_2O \rightarrow CaCO_3+2\ NH_3.$$

This gives opportunity to use the ammonia for direct oxidation to nitric acid. The cyanamide yields soluble nitrogen compounds when in contact with the moisture of the soil, hence it may be used as a fertilizer. ***Calcium bisulfite,*** $Ca(HSO_3)_2$, made by passing rather pure sulfur dioxide into a suspension of lime, is of great importance in the manufacture of paper pulp.

Hardness of Water.[1] — Natural waters in contact with deposits of limestone or dolomite dissolve appreciable amounts of these rocks if carbon dioxide be present, as it always is. The soluble bicarbonates of calcium and magnesium formed give *temporary hardness* to the water, temporary because on heating, these bicarbonates decompose with precipitation of the normal carbonates.

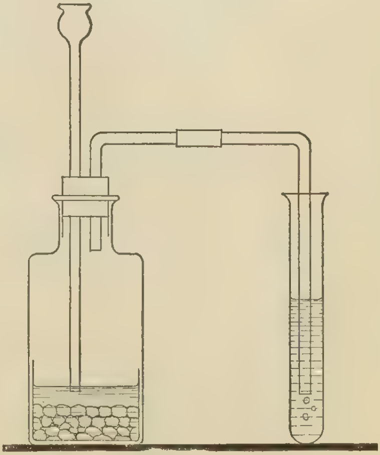


FIG. 98

Pass carbon dioxide into clear lime water (Fig. 98). A precipitate of the carbonate forms. An excess of carbon dioxide dissolves this precipitate—the water has acquired temporary hardness. Now boil the solution and note the formation of insoluble calcium carbonate, not by evaporation but merely by raising the temperature.

$$\begin{aligned}&(1)\ Ca(OH)_2+CO_2 \rightarrow CaCO_3+H_2O\\&(2)\ CaCO_3+H_2CO_3 \rightarrow Ca(HCO_3)_2\\&(3)\ Ca(HCO_3)_2 \rightarrow CaCO_3+H_2O+CO_2\end{aligned}$$

Permanent hardness is due largely to calcium and magnesium sulfates, which are not precipitated by mere boiling, unless the solution is made very concentrated by evaporation. A comparison of solubilities at ordinary temperatures is interesting.

---

[1] In Cady's *Inorganic Chemistry*, page 425, is given a good discussion of methods of determining the proper amounts of softeners to add to hard water.

Permanent hardness	1 liter of water dissolves	0.013 g. $CaCO_3$
	1 liter of water dissolves	1.000 g. $MgCO_3$
	1 liter of water dissolves	2.000 g. $CaSO_4$
	1 liter of water dissolves	354.000 g. $MgSO_4$

As a matter of fact, no natural water contains enough magnesium bicarbonate to cause precipitation of magnesium carbonate (solubility, 1 g. per liter) on boiling without evaporation. In certain districts some of the temporary hardness is due to ferrous bicarbonate, $Fe(HCO_3)_2$.

Hardness in commercial practice in this country is measured in grains per gallon. That is, one degree of hardness (U. S.) is 1 grain per gallon (0.017 gram per liter). In scientific work the French system is used. One part of $CaCO_3$ (or its equivalent) per 100,000 parts of water (0.01 gram per liter) is one degree of hardness. Water below 5 degrees is soft and above 30 degrees very hard.

Softening Water. — The importance of softening water is great. In boilers a hard scale of salts is left by the evaporation of feed water. This scale is a poor conductor of heat and causes a serious waste of fuel. A layer one eighth inch thick causes a loss of 10–12 per cent of fuel. This loss increases as the square of the thickness. Furthermore superheating of the boiler may result. Cracking of the brittle scale may admit water to the overheated iron, causing an explosive generation of steam. If the temperature of the iron rises too high a layer of the oxide, Fe_3O_4, forms, weakening the boiler to the danger point.

Hardness of water causes an appalling waste of soap. No lather can form and consequently no cleansing be achieved until all the hardness has been precipitated at the expense of the soap. Thus, with sodium oleate, representing a typical soap, we have:

$$2\ Na.Oleate + CaSO_4 \rightarrow Na_2SO_4 + Ca.Oleate.$$

A further annoyance is caused by the stickiness of the calcium oleate formed. All calcium soaps are insoluble and curdy.

The hardness of city water in Los Angeles is 25 degrees (United States), in Dayton 22 degrees, in Indianapolis 17 degrees, in Chicago 8 degrees, and in New York only 2.5 degrees. If 6 pounds of soap are wasted with every 100 gallons of water of 35 degrees hardness, the total cost of water hardness in some of these cities must be impressive.

One of the cheapest softeners is lime itself. This sounds to the public like making matters worse, for it is often said that "lime causes the hardness of water." However, the following equations show the explanation of the paradox:

(1) $Ca(HCO_3)_2+Ca(OH)_2 \rightarrow 2\,H_2O+2\,CaCO_3\downarrow$
(2) $Fe(HCO_3)_2+Ca(OH)_2 \rightarrow 2\,H_2O+CaCO_3\downarrow+FeCO_3\downarrow$
(3) $MgCO_3+Ca(OH)_2 \rightarrow CaCO_3\downarrow+Mg(OH)_2\downarrow.$

Reaction (3) is worthy of special attention. Either the bicarbonate or normal carbonate of magnesium is converted by any base into the decidedly insoluble hydroxide. Remember that one liter of water dissolves 1 g. of $MgCO_3$ but only 0.01 g. of $Mg(OH)_2$. To precipitate permanent hardness crude "soda ash" is used:

$$CaSO_4+Na_2CO_3 \rightarrow Na_2SO_4+CaCO_3\downarrow.$$

Sodium hydroxide is not as cheap, but it takes care of both kinds of hardness because the sodium carbonate produced in the following reaction reacts with the permanent hardness as indicated above:

$$Ca(HCO_3)_2+2\,NaOH \rightarrow H_2O+CaCO_3\downarrow+Na_2CO_3.$$

The common practice to-day is to use both lime and soda ash, varying the proportions with the seasonal variations in the water content. Trisodium phosphate is used somewhat as a softener. It is powerfully alkaline by hydrolysis and in addition causes formation of insoluble phosphates.

Boiler compounds usually consist of soda ash or sodium phosphate with tannic acid, starch or some gummy material (protective colloid) that prevents the formation of a hard, compact scale. Graphite or talc are added by some engineers for the same purpose, but their use is questionable. A loose scale can be blown out at intervals. Boiler compounds are introduced in the boiler, but it is much better to soften the water outside the boiler in settling tanks.

The very modern ***permutit process*** (Fig. 99) of softening yields water of zero degrees of hardness. No other chemical will do this in practice. An artificial zeolite (really a sodium silico-aluminate) is prepared and never allowed to lose its porous structure by drying. When hard water slowly flows through a bed of this Na. Permutit there is an exchange of calcium and magnesium for sodium:

$$Ca(HCO_3)_2 + 2Na.Permutit \rightarrow 2NaHCO_3 + Ca(Permutit)_2.$$

After a time the permutit no longer functions, having become Ca.Permutit. Salt water (10 per cent) is then left on it for about 12 hours and, because the sodium chloride is now in excess, the Na.Permutit is regenerated. After washing out the salt it is ready for use again:

$$Ca(Permutit)_2 + 2NaCl \rightarrow CaCl_2 + 2Na.Permutit.$$

This reaction is really reversible, depending only on whether the sodium chloride or a soluble calcium salt is in excess. The value of the perfectly soft water produced by the permutit process is so great to the dye industry, the textile industry, and hotel or household systems, that, in spite of its extra cost, installations are very numerous. The active material can be used and regenerated twenty years or longer.

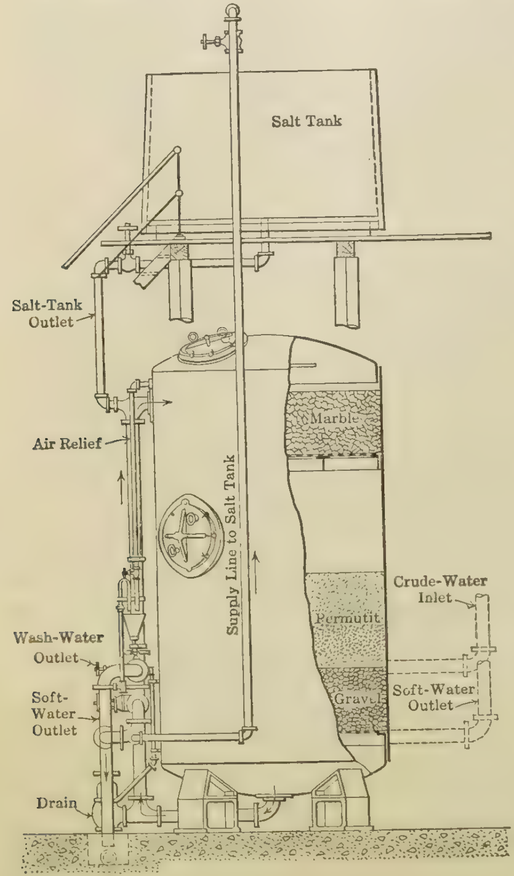


Fig. 99

In the laundry it is best to soften the water with soda, borax or trisodium phosphate *before* adding any soap. The sticky curds of calcium soaps, for example, soil the clothes and are hard to remove. Preliminary softening prevents this. Iron soaps, if not removed, would finally cause rusting spots. The cleansing action of soap was discussed in the chapter on Colloid Chemistry under Adsorption.

Tests for Calcium Compounds. — The calcium flame is brick-red, but the extreme insolubility of white calcium oxalate is usually taken as the best test.

BARIUM

Occurrence. — The chief barium mineral is barite, $BaSO_4$. In 1915 the United States produced 108,547 tons of this rock. Witherite, $BaCO_3$, is not so common.

Barium Sulfate, $BaSO_4$. — This mineral is the starting point for the preparation of all barium compounds, including the precipitated form of barium sulfate. Coal mixed with four times its weight of barite is roasted four hours in a rotating furnace. The barium sulfide formed is treated with water. It is not very soluble, but is slowly hydrolyzed to the more soluble hydrosulfide. By reaction with "salt cake," Na_2SO_4, the finely divided "blanc fixe" or precipitated barium sulfate is formed:

$$BaS + Na_2SO_4 \rightarrow Na_2S + BaSO_4.$$

The sodium sulfide is a by-product necessary in making and using sulfur dyes. Blanc fixe is used, when pure white, as the body of lithograph inks, and lake colors and as filler for paints, rubber, linoleum, oilcloth and glazed paper.

The barium sulfide may be made to react with a solution of sodium carbonate to form the "precipitated" barium carbonate, which is, of course, a finer powder than ground witherite:

$$BaS + Na_2CO_3 \rightarrow Na_2S + BaCO_3.$$

By direct heating of barite, coal and calcium chloride, the valuable barium chloride is secured. Of course the coal first reduces the sulfate:

$$BaSO_4 + 2\ C + CaCl_2 \rightarrow BaCl_2 + 2\ CO_2 + CaS.$$

Reaction of the sulfide with a solution of sodium nitrate yields barium nitrate, from which the oxides are prepared. Barium sulfide is mixed with zinc sulfate solution to form lithopone, a valuable paint:

$$BaS + ZnSO_4 \rightarrow BaSO_4 + ZnS.$$

The Barium Oxides. — The monoxide is sometimes made by heating the nitrate:

$$2\,Ba(NO_3)_2 \rightarrow 2\,BaO + 4\,NO_2 + O_2.$$

It is also prepared by roasting the carbonate. However, barium carbonate is much more stable than calcium carbonate and must be heated above 1350° to secure rapid dissociation. The corresponding temperature for calcium carbonate is 898°. By heating barium carbonate with carbon the carbon dioxide is constantly removed by reduction to carbon monoxide. This lowers the partial pressure of the dioxide and thus facilitates decomposition of the carbonate:

$$BaCO_3 \leftrightarrows BaO + CO_2,$$
$$CO_2 + C \rightarrow 2\,CO.$$

Barium oxide was once of interest in connection with the Brin process of making oxygen. It is now important mainly in preparing the dioxide by heating in air above 500°:

$$2\,BaO + O_2 \leftrightarrows 2\,BaO_2.$$

This equilibrium is disturbed by change in temperature or in pressure. The dissociation pressure of the peroxide at 790° is 670 mm. Therefore, according to W. A. Noyes, if heated in the open air the peroxide decomposes at that temperature because only one fifth the pressure of air is due to oxygen ($\frac{760}{5} = 152$ mm.). This back pressure of oxygen is not enough to prevent decomposition, but if five atmospheres air pressure be applied, that due to oxygen will now be 760 mm., more than enough to prevent decomposition. In fact, under these conditions oxygen will add on to the monoxide. At 670° the dissociation pressure of barium peroxide is only 80 mm., so even in the open air the peroxide can be formed readily from the monoxide.

Barium peroxide is important now as a source of hydrogen peroxide. Almost any acid can be used in reaction with the barium compound, but in practice carbonic, sulfuric and phosphoric are found most suitable. Since soluble barium salts are poisonous, hydrochloric acid will not do, as it would leave barium chloride in solution:

$$BaO_2 + H_2SO_4 \rightarrow H_2O_2 + BaSO_4 \downarrow.$$

Barium Hydroxide, $Ba(OH)_2$. — The hydroxide of barium is much more soluble than either calcium or strontium hydroxide. It is a moderately strong base and is used in quantitative analysis to absorb carbon dioxide.

Other Barium Compounds. — The nitrate, $Ba(NO_3)_2$, is used in green pyrotechnic signals and in some explosives. Its chief use is in manufacture of the oxides. The chloride, $BaCl_2$, has some use as a mordant for dyes and as a water softener. The chlorate is mixed with sulfur and charcoal to produce green fire.

Exercise 5. — Draw a chart like that given for cyanamide (page 404), to show the derivatives of the mineral barite.

Tests for Barium Compounds. — The barium flame is green (distinctive except for copper and boric acid). The usual tests involve the precipitation of yellow barium chromate and white barium sulfate, insoluble in dilute acids.

STRONTIUM

Occurrence. — The chief ores of strontium, like those of calcium and barium, are the carbonate, $SrCO_3$, and sulfate, $SrSO_4$. The sulfate, celestite, occurs in beautifully crystallized masses in a cave near Put-in-Bay and at other points along Lake Erie. The carbonate, strontianite, is not so plentiful.

Strontium Nitrate, $Sr(NO_3)_2$. — This salt is mixed with sulfur, charcoal, and potassium chlorate to make red lights for signals or fireworks. Like most strontium compounds it is made by reduction of the sulfate with hot carbon and treatment of the strontium sulfide formed with the appropriate acid or salt.

Strontium Hydroxide, $Sr(OH)_2$. — The base is by far the most important strontium compound. It may be produced by heating the carbonate in a current of superheated steam:

$$SrCO_3+H_2O \rightarrow CO_2+Sr(OH)_2.$$

In Europe large quantities are used in purifying beet sugar. To the sugar molasses heated above 100°, strontium hydroxide is added. This reacts with the sugar, forming crystals of strontium disucrate. These are filtered off, washed and dissolved in a cold solution of strontium hydroxide. After standing several days half of the strontium hydroxide crystallizes out. Carbon dioxide is then passed into the solution. Strontium carbonate is precipitated, leaving the sugar in solution, free from all impurities. On evaporation in the vacuum pans a good grade of sugar is secured, needing no further refining.

Tests for Strontium Compounds. — The characteristic carmine red flame is an indicator of strontium. Precipitation of its carbonate, sulfate and oxalate, all white salts, aids in testing for the element.

CHAPTER XXIX

EQUILIBRIUM

On page 53 the reversible reaction

$$(1)\ Fe_3O_4+4\ H_2 \leftrightarrows 3\ Fe+4\ H_2O$$

was discussed as an example of chemical equilibrium. Another reversible reaction mentioned as of great importance was the following:

$$(2)\ Cl_2+H_2O \leftrightarrows HCl+HClO.$$

In connection with the latter reaction it was stated that in the sunlight the hypochlorous acid decomposes so that the equilibrium is steadily disturbed towards the right. Naturally if the hypochlorous acid were no longer present it could not react with the hydrochloric acid to form any more chlorine and water. In other words, removal of one product disturbs equilibrium in the direction favoring formation of more of that product. The same result is achieved by addition of a base, which, of course, neutralizes the acids, thus suppressing completely any reaction to the left.

It has been stated that escape of a product as a gas prevents reversion of a reaction and so such reactions proceed to completion. This may occur quite simply, as in the attack of an acid on a metal or on a carbonate:

$$Zn+H_2SO_4 \rightarrow ZnSO_4+H_2 \uparrow$$
$$CaCO_3+2\ HCl \rightarrow CaCl_2+H_2O+CO_2 \uparrow$$

To be exact, there are some of these reactions which would not be reversed even if the escape of a gas were prevented by suitable means. There must be some affinity (tendency to react) between the products or no reaction occurs.

In equation (1) this removal of one product as a gas may be brought about if the iron oxide be heated in a tube open at both ends while a stream of hydrogen is passed through. This hydrogen stream steadily removes water as fast as formed and the equilibrium, such as might exist in a closed tube, is continuously disturbed to the right. The student should read again the discussion of this reaction on page 53. Another device to secure the removal of one product as a gas is to heat to a suitable temperature. For example, nitric acid is often prepared by heating a mixture of concentrated sulfuric acid and sodium nitrate. Care is taken to heat only above the boiling point of the nitric acid but not above the boiling point of sulfuric acid:

$$\mathrm{NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3} \uparrow .$$

On page 113 the preparation of hydrogen chloride from concentrated sulfuric acid and sodium chloride is described. The hydrogen chloride escapes because it is insoluble in concentrated sulfuric acid:

$$\mathrm{NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl} \uparrow .$$

However, if dilute sulfuric acid be used no gas escapes, even on warming. The great solubility of hydrogen chloride in water keeps it in contact with the sodium hydrogen sulfate and reaction follows. Thus an equilibrium involving four substances results.

$$\mathrm{NaCl + H_2SO_4 \leftrightarrows NaHSO_4 + HCl_4}.$$

All ionization reactions involve equilibria which may be disturbed in one direction or the other by dilution or concentration:

$$\mathrm{NaCl} \leftrightarrows \overset{+}{\mathrm{Na}} + \overset{-}{\mathrm{Cl}}.$$

Here again such reactions may be made to proceed to completion by removal of one of the products. This could be accomplished very simply in the case of sodium chloride by addition of any positive ion capable of uniting with the chloride ion to form an insoluble compound. Silver ion (from a solution of silver nitrate, for example) unites with chloride ion, forming insoluble silver chloride, and thus forces complete progressive ionization of all the sodium chloride molecules:

$$\begin{array}{rcccl}
\mathrm{NaCl} \leftrightarrows & \overset{+}{\mathrm{Na}} & + & \overset{-}{\mathrm{Cl}} & \\
\mathrm{AgNO_3} \leftrightarrows & \overset{-}{\mathrm{NO_3}} & + & \overset{+}{\mathrm{Ag}} & \\
 & \downarrow\uparrow & & \downarrow & \\
 & \mathrm{NaNO_3} & & \mathrm{AgCl} & \downarrow .
\end{array}$$

It is not always necessary even to remove an ion in the form of a precipitate or a gas. It may possibly react with another ion to form a slightly ionized substance such as water or a weak acid or base.

$$HCl \leftrightarrows \overset{+}{H} + \overset{-}{Cl}$$

$$\begin{array}{ccccc} NaOH & \leftrightarrows & \overset{-}{OH} & + & \overset{+}{Na} \\ & & \downarrow & & \downarrow\uparrow \\ & & H_2O & & NaCl. \end{array}$$

The neutralization of an acid by a base, as outlined above, is not a reaction between molecules but between ions. The removal of $\overset{+}{H}$ ion and $\overset{-}{OH}$ ion from the solution forces the complete ionization of all molecules of the original substance.

Exercise 1. — Give an illustration showing how an ionic equilibrium can be disturbed by tying up one of the ions in molecules of a weak acid. Of a weak base.

Exercise 2. — The preparation of a pure compound by double decomposition depends upon a choice of reacting ions such that the reaction shall proceed to completion or nearly so. Give examples of different ways in which this may be done.

Since any positive ion attracts and discharges any negative ion, there is no question of any lack of chemical affinity when solutions of electrolytes are mixed.

Effect of Change in Temperature. — All reactions increase in speed with rise in temperature, but such increase is not the same in all cases. Thus one reaction in an equilibrium condition may be accelerated more than the opposing reaction. As a result the equilibrium would be disturbed and a new adjustment of velocities reached. That reaction will be favored which absorbs heat. (See *Principle of Le Chatelier.*) For example: Deacon's process of making chlorine from hydrogen chloride works best at a moderate temperature.

$$(1)\quad 4\,HCl + O_2 \rightarrow 2\,H_2O + 2\,Cl_2 + 28{,}000 \text{ cal.}$$
$$(2)\quad 2\,H_2O + 2\,Cl_2 \rightarrow 4\,HCl + O_2 - 28{,}000 \text{ cal.}$$
$$(3)\quad 4\,HCl + O_2 \leftrightarrows 2\,H_2O + 2\,Cl_2.$$

A rise in temperature favors reaction (2) more than (1) and must disturb the existing equilibrium of (3). Of course some heating is necessary to secure sufficient velocity of reaction.

Effect of Change in Pressure. — Any increase in pressure on a system in equilibrium tends to bring reacting particles in closer contact and to compress the products. Consequently the formation of substances occupying a smaller volume will be favored. For example, one volume of nitrogen reacts with three volumes of hydrogen to form only two volumes of ammonia:

$$N_2+H_2+H_2+H_2 \leftrightarrows 2\,NH_3.$$

In Haber's process great pressure is applied because pressure favors the formation of two volumes of ammonia from a total of four volumes of nitrogen and hydrogen. It goes without saying that high pressure must oppose the expansion involved in the decomposition of ammonia into its elements. This is another application of the Principle of Le Chatelier.

Effect of a Catalyst. — The effect of a catalyst is merely to bring about equilibrium more quickly. This is commercially important, for some opposing reactions do not come to a definite equilibrium for months unless hurried by a catalyst. If a catalyst could really disturb an existing equilibrium, it would be possible to get work done without any expenditure of energy by alternately removing and putting back the catalyst — a scientific impossibility.

The Law of Mass Action. — The speed of a reaction is proportional to the molecular concentration of the reacting substances and is also influenced by the nature of the molecules involved. (By a concentration of "1" we mean one gram-molecular weight per liter.) With solids and homogeneous liquids such concentration changes are not to be expected as with gases and substances in solution. Consider a reaction between two gases, A and B, in equilibrium with C and D:

$$A+B \leftrightarrows C+D.$$

Suppose we have, in a unit volume, just 1,000,000 molecules of A and an equal number of B. At a given temperature, etc., the speed of reaction to the right will be definite. But if we double the concentration of A, use 2,000,000 molecules per unit volume without changing B, it is obvious that the speed of reaction will be doubled because there will be just twice as many contacts per second between A and B as before. If we treble the concentration of B, take 3,000,000 molecules per unit volume, the previous speed of reaction must be trebled, due to three times as many contacts per second as before. The final speed must be six times the original speed since it was once doubled and that speed immediately trebled.

The same facts may be expressed in another way. Let the molecular concentration of A (number of gram-molecular weights per liter) be represented by [A] and the molecular concentration of B by [B]. Since the velocity of reaction is proportional to the concentration of A and also of B, it must be proportional to their product:

$$[A] \times [B] \propto \text{speed}.$$

Now it isn't really true that the number represented by this product equals the number of gram-molecular weights of C and D formed per second (the speed). We merely mean to say that the speed changes proportionately to any change in this product. We should, however, be justified in introducing a factor peculiar to the reaction, letting it represent all the other influences affecting a reaction. [A] and [B] represent the concentration influence only, but we must remember that temperature, affinity and catalysis have an effect. Combine all but the concentration influence in "k," which remains constant during any changes in concentration:

$$[A] \times [B] \times k = \text{speed}$$

The speed of reaction between hydrogen and iodine is represented in exactly the same way:

$$[H_2] \times [I_2] \times k = \text{speed}.$$

It is not so simple in the case of the reaction between hydrogen and oxygen. We can approach this question by imagining three reacting substances, A, B and C:

$$[A] \times [B] \times [C] \times k = \text{speed}.$$

Suppose B to be identical with A. Then the statement becomes

$$[A] \times [A] \times [C] \times k = \text{speed},$$

$$\text{or} \quad [A]^2 \times [C] \times k = \text{speed}.$$

Applying this logic to the reaction between hydrogen and oxygen we may write the following:

$$H_2+H_2+O_2 \rightarrow 2\ H_2O,$$
$$[H_2]\times[H_2]\times[O_2]\times k=\text{speed},$$
$$[H_2]^2\times[O_2]\times k=\text{speed}.$$

Application to an Equilibrium Reaction. — Let us assume that the reaction discussed is reversible:

$$A+B \leftrightarrows C+D.$$

Without further discussion it is evident that the speed of reaction to the left is proportional to the molecular concentration of C and D, and to a constant factor k′ peculiar to that reaction:

$$\text{speed}=[C]\times[D]\times k'.$$

When equilibrium is reached the two speeds are equal:

$$[A]\times[B]\times k=[C]\times[D]\times k'$$

By a simple algebraic process we may transform this into a more useful statement:

$$\frac{[A]\times[B]}{[C]\times[D]}=\frac{k'}{k}=K.$$

Since both k and k′ were constant factors, despite the changes in concentration, the quotient $\frac{k'}{k}$ must also be a constant value represented by K. The convenient phrase "equilibrium constant" is applied to K.

An illustration of the application of the equilibrium constant may be found in the conditions in chlorine water:

$$Cl_2+H_2O \leftrightarrows HCl+HClO$$
$$[Cl_2]\times[H_2O]\times k=\text{speed to right}$$
$$\text{Speed to left}=[HCl]\times[HClO]\times k'$$
$$[Cl_2]\times[H_2O]\times k=[HCl]\times[HClO]\times k'$$
$$\frac{[Cl_2]\times[H_2O]}{[HCl]\times[HClO]}=K.$$

Applications to Ionic Equilibrium. — It is very interesting to formulate and compare equilibrium constants for acids and bases. Here we begin to see some reason for the preceding drill. Consider a typical strong acid such as hydrochloric and a typical weak acid such as acetic:

$$\mathrm{HCl} \leftrightarrows \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{Cl}}$$

$$\frac{[\overset{-}{\mathrm{H}}] \times [\overset{-}{\mathrm{Cl}}]}{[\mathrm{HCl}]} = \mathrm{K}$$

$$\mathrm{H.C_2H_3O_2} \leftrightarrows \overset{+}{\mathrm{H}} + \overset{-}{\mathrm{C_2H_3O_2}}$$

$$\frac{[\overset{+}{\mathrm{H}}] \times [\overset{-}{\mathrm{C_2H_3O_2}}]}{[\mathrm{H.C_2H_3O_2}]} = \mathrm{K'}$$

The equilibrium (or ionization) constant, K, for hydrochloric acid is relatively much greater than the similar constant K′, of an acetic acid solution of equal concentration. Strong acids are highly ionized in dilute solution so the numerator in such a fraction as $\frac{[\overset{+}{\mathrm{H}}] \times [\overset{-}{\mathrm{Cl}}]}{[\mathrm{HCl}]}$ is much larger than the denominator. In a 0.1 N solution of hydrochloric acid only 7 per cent of the acid is present in the form of molecules, and consequently the molecular concentration of the ions is about 13 times as great as the figure for the molecules. In 0.1 N solution of acetic acid fully 96 per cent of the molecules are not ionized, so the molecular concentration of acetic acid is over 24 times as great as the concentration of its ions. From this comparison we learn that "K" for weak acids is a very small number and for strong acids is relatively large. A similar statement holds for bases.

To calculate the ionization constant for an electrolyte we need only measure by suitable means the percentage of ionization and substitute the proper values in the formula. In a 0.1 N solution of hydrochloric acid the molecular concentration of HCl would be 0.1 if none of the molecules were ionized. However, only 7 per cent of this concentration remains in molecular form. (See page 148.) From all HCl molecules ionized there comes an equal number of $\overset{+}{\mathrm{H}}$ ions and $\overset{-}{\mathrm{Cl}}$ ions. Thus the molecular concentration of the $\overset{+}{\mathrm{H}}$ ions or the $\overset{-}{\mathrm{Cl}}$ ions must be $0.93 \times 0.1 = 0.093$ and the molecular concentration of the nonionized molecules must be $0.07 \times 0.1 = .007$. Substituting these values we find K to be about 1, as it is for all strong acids and bases. At other concentrations this value of K varies widely, so it is incorrect to speak of a *constant* value of K for well-ionized electrolytes:

$$\frac{[\overset{+}{\mathrm{H}}]\times[\overset{-}{\mathrm{Cl}}]}{[\mathrm{HCl}]}=\mathrm{K} \text{ or } \frac{[0.093]\times[0.093]}{[0.007]}=1.2356.$$

The ionization constant for acetic acid is only 1.8×10^{-5}, and for hydrocyanic acid (HCN) it is 7×10^{-10}. For all weak acids and bases the value of K is constant.

Effect of Dilution. — Suppose a molar solution of an acid AB is exactly 50 per cent ionized. The concentration of the non-ionized molecules must be 0.5 and the concentration of each ion also 0.5. Substituting in the formula we get the value 0.5 for K.

$$\frac{[0.5]\times[0.5]}{[0.5]}=\frac{0.25}{0.5}=0.5.$$

On addition of an equal volume of water the concentrations must all be halved, if no further ionization occurred:

$$\frac{[0.25]\times[0.25]}{[0.25]}=0.25.$$

But with increasing dilution a greater percentage of the molecules ionize, thus decreasing the numerical value of the denominator and increasing the value of the numerator. This adjustment is found, by actual laboratory observation, to be such that the value of the fraction remains constant, at 0.5 for K. Dilution does not change the ionization constant.

Effect of a Common Ion. — Acetic acid is a weak acid but more than sufficiently ionized to turn methyl orange red. If to such a red solution considerable of sodium acetate be added, the color changes to yellow, indicating a great suppression of $\overset{+}{\mathrm{H}}$ ion:

$$\frac{[\overset{+}{\mathrm{H}}]\times[C_2H_3O_2]}{[H.C_2H_3O_2]}=\mathrm{K}.$$

Sodium acetate, like all soluble salts, ionizes very well, but acetic acid yields relatively few ions. Addition of much sodium acetate, therefore, greatly increases the concentration of the acetate ion in the equilibrium for acetic acid. Apparently this must increase the numerical value of the numerator in the above fraction, yet actual laboratory measurements show that K has not changed. The explanation is simple: any increase in the concentration of acetate ions affords more opportunities for contact with hydrogen ions, thus decreasing the concentration of hydrogen ions since they are tied up to some extent in the molecules of acetic acid thus formed. Suppose the concentration of acetate ions were increased 100 times. We might conclude that the concentration of hydrogen ions must be decreased to one hundredth of its previous value, but the value of $[\text{H.C}_2\text{H}_3\text{O}_2]$ is also increasing. The fact is, all values adjust themselves so as to maintain K as a constant. Addition of potassium acetate would suppress the ionization of acetic acid in the same way.

However, an attempt to suppress the ionization of a strong acid like hydrochloric by addition of sodium chloride doesn't amount to much. The principle applies but there are too many hydrogen ions to suppress readily.

Precipitation Conditions. — In a *saturated* solution of any salt the concentration of the dissolved molecules must itself be a constant value. Otherwise more solid would dissolve or a precipitate would form and the solution could not have been saturated. Therefore, the variable [dissolved molecules] becomes a constant value and may be joined to the ionization constant.

The expression, $\dfrac{\overset{+}{[\text{Na}]}\times\overset{-}{[\text{Cl}]}}{[\text{NaCl}]}=\text{K}'$, for an unsaturated solution becomes $\dfrac{\overset{+}{[\text{Na}]}\times\overset{-}{[\text{Cl}]}}{\text{k}}=\text{K}'$ for a saturated solution. By an algebraic process this changes to a simpler form:

$$\overset{+}{[\text{Na}]}\times\overset{-}{[\text{Cl}]}=\text{K}'\times\text{k}=\text{K}.$$

For very soluble electrolytes this value, K, must be relatively large. For an insoluble salt like barium sulfate, K must be minute, since in a saturated solution of barium sulfate (1 g. per 400,000 cc.) there are too few $\overset{++}{\text{Ba}}$ ions or $\overset{--}{\text{SO}_4}$ ions to yield an ion product worth mentioning. Evidently the value of K for saturated solutions is a direct measure of solubility, hence the name *solubility product.* To secure precipitation we need only increase the concentration of either ion (or of both) concerned to such a point that the product shall exceed K for a saturated solution of that electrolyte.

Sodium chloride is reasonably soluble and yet if into a saturated solution of that salt some hydrogen chloride gas be passed, crystals of sodium chloride settle out:

$$[\overset{+}{Na}]\times[\overset{-}{Cl}]=K.$$

The increase in value of $[\overset{-}{Cl}]$ due to addition of HCl without dilution causes an increase in the product. But K is always constant, therefore $[\overset{+}{Na}]$ must decrease to keep this value of K the same. But an increase of $[\overset{-}{Cl}]$ and decrease of $[\overset{+}{Na}]$ means the formation of NaCl molecules. Since the solution is already saturated a precipitate forms.

With a very low concentration of $\overset{++}{Cu}$ ions in a solution there need be added only a small concentration of $\overset{--}{S}$ ions to exceed the extremely small solubility product of copper sulfide:

$$[\overset{++}{Cu}]\times[\overset{--}{S}]=k.$$

The converse of the above must be that whenever the product of the concentrations of any two ions in a saturated solution is made less than the actual solubility product of this compound, any undissolved substance present must dissolve. If to a suspension of $Fe(OH)_3$ any acid be added, the precipitate dissolves:

$$\overset{\text{Undissolved}}{Fe(OH)_3} \leftrightarrows \overset{\text{Dissolved}}{Fe(OH)_3} \leftrightarrows \overset{+++}{Fe}+\overset{-}{OH}+\overset{-}{OH}+\overset{-}{OH}.$$

The $\overset{+}{H}$ ions of the acid unite with $\overset{-}{OH}$ ions to form water. Consequently the product of the concentrations of the $\overset{+++}{Fe}$ ions and $\overset{-}{OH}$ ions falls below the solubility product and more precipitate must dissolve.

Equilibrium in Acidic and Basic Solutions. — As shown by the facts of hydrolysis there is an equilibrium in pure water:

$$\overset{+}{H}+\overset{-}{OH}\leftrightarrows H_2O.$$

Addition of an acid disturbs this equilibrium to the right and decreases the concentration of $\overset{-}{\mathrm{OH}}$ ions, perhaps almost to the vanishing point. Addition of a base to water also disturbs the equilibrium to the right but decreases the concentration of $\overset{+}{\mathrm{H}}$ ions. In each case it is a matter of addition of a common ion, either $\overset{+}{\mathrm{H}}$ ions or $\overset{-}{\mathrm{OH}}$ ions. "Mass action" expresses it. It is usual for us to think of an acid solution as marked by the presence of $\overset{+}{\mathrm{H}}$ ions and entire absence of $\overset{-}{\mathrm{OH}}$ ions. Such is not the case. An acidic solution is merely one in which there are *more* $\overset{+}{\mathrm{H}}$ ions than $\overset{-}{\mathrm{OH}}$ ions.

Some indicators change color when the excess of $\overset{+}{\mathrm{H}}$ ions reaches a definite concentration. For example, methyl orange does not change from yellow to pink until there are present a million times as many $\overset{+}{\mathrm{H}}$ ions as $\overset{-}{\mathrm{OH}}$ ions.

Exercise 3. — What is the effect of adding ammonium chloride to a solution of ammonium hydroxide?

CHAPTER XXX

COPPER, SILVER, AND GOLD

The Group. — A glance at the periodic table reminds the student that Group I is made up of two families of metals. Placed on the left of the column are the alkali metals, while copper, silver and gold are placed on the right. The most striking resemblance between the two sub-groups is in their common valence of one. Yet copper and gold have two valences. The alkali metals are strongly basic while copper and gold are weakly basic. Silver hydroxide is a strong base, but it is only slightly soluble.

The alkali metals are very soft, very light, melt at rather low temperatures and are extremely active chemically. In these respects the other sub-group is distinctly different. Copper, silver and gold are much harder, far heavier and all three melt near 1000°. They are so inactive they do not react with water and, in fact, do not displace hydrogen from acids. Copper forms a very thin film of oxide in air, but gold and silver are not affected by air. This inactivity explains the occurrence of these three metals free in nature. Consequently they were known in ancient times. Their beauty made them especially desirable.

COPPER

Occurrence. — The world produces 1,000,000 tons of copper annually and of this total the United States furnishes over one half. England, Japan, Spain, Germany, Chili, Mexico, and Siberia supply the rest. A large deposit of free copper occurs in Michigan around Lake Superior, but the chief ores are chalcocite, Cu_2S, and copper pyrites, $CuFeS_2$, found in Montana and Utah. Malachite, $Cu_2(OH)_2CO_3$, occurs in Arizona. Tennessee and Alaska also possess great deposits of rich copper ores.

The military importance of a sufficient supply of domestic copper ores was convincingly demonstrated by Germany's plight during the Great War. Her own supply was inadequate.

Metallurgy. — The separation of native copper from the surrounding rock is largely mechanical. After grinding and washing the ore is melted with a flux (to lower the melting point of the waste rock). The heavier melted copper is easily separated.

Sulfide ores require a different treatment. They usually contain more or less iron. In general such ores are roasted to burn out the sulfur. The iron oxide resulting reacts with added sand to form the fusible slag, ferrous silicate. For detailed modern methods we can do no better than consider the process used near Butte, Montana. Here in an area of three or four square miles one tenth of all the copper produced by the world is mined. It is smelted a few miles away at Anaconda.

Obviously, ores containing three per cent copper must be concentrated before smelting, and this is done by a series of grinding and washing operations. The product, carrying eight per cent copper, is next *roasted* to remove 80 per cent of the sulfur. Some sulfide is necessary to permit the formation of "matte." After a roasting furnace is started no more fuel is needed because the heat of the burning sulfur is sufficient. The charge is brought to a red heat but not allowed to melt.

After roasting the hot charge is introduced into enormous *reverberatory furnaces*, usually about 20 ft. wide and 100 ft. long. These furnaces are lined with silica brick and have arched roofs to radiate heat down on the charge. The floor, however, is of magnesite. They are fired with powdered coal blown in by a jet of compressed air. Some silica and alumina are left in the charge from the original ore, but limestone is added to aid in the formation of a fusible slag. Much iron is removed in the slag. A heavy molten mixture of sulfides of copper and iron called "matte" is removed and taken to the converters, where a blast of air burns out the remaining sulfur and oxidizes the iron and other impurities. A converter is made of a shell of heavy steel plate lined with magnesite brick. The inside dimensions are usually 16 feet diameter and 15 feet depth although the Anaconda converters are 20 ft. wide. At the back and near the bottom a line of tuyère pipes admit compressed air. The iron oxide formed combines with silica and alumina of some raw ore added for this purpose to form slag which is poured off by tilting the converter. The 65-ton charge of matte is blown about 5 hours, while the Bessemer converter used in steel making is blown only 15 minutes. The converter reactions are represented by the following equations:

$$\begin{aligned}&2\,\mathrm{FeS}+3\,\mathrm{O_2} \rightarrow 2\,\mathrm{FeO}+2\,\mathrm{SO_2}+221{,}920\text{ cal.},\\&\mathrm{FeO}+\mathrm{SiO_2} \rightarrow \mathrm{FeSiO_3},\\&2\,\mathrm{Cu_2S}+3\,\mathrm{O_2} \rightarrow 2\,\mathrm{Cu_2O}+2\,\mathrm{SO_2},\\&\mathrm{Cu_2S}+2\,\mathrm{Cu_2O} \rightarrow 6\,\mathrm{Cu}+\mathrm{SO_2}.\end{aligned}$$

The converter product, 99 per cent blister copper, is then cast into heavy plates for electrolytic refining.

The Flotation Process: — Former methods of concentrating the crushed ores left considerable copper in the rejected tailings. By the modern flotation process these tailings are worked over with great profit. Finely ground ore is stirred with water and less than one per cent of oil so that an oily froth forms when air is blown or beaten into the pulp. The valuable copper sulfide particles are wet by the oil more than by water so they are floated in the froth while the waste rock or gangue, which is preferentially wetted by water, sinks. The froth is removed and its load of rich ore recovered. This is one of the most sensational developments in modern metallurgy. Sixty million tons of ore are concentrated yearly by the flotation process.

Electrolytic Refining. — Since the leading use of copper (as a conductor of electricity) demands a metal 99.95 per cent pure, it is necessary to remove all but traces of the arsenic, lead, silver, gold and zinc impurities. Only 0.03 of one per cent arsenic lowers the conductivity of copper about 14 per cent. The slabs of cast copper from the smelters are made anodes in a bath of copper sulfate acidified with sulfuric acid. The cathodes are very thin sheets of pure copper arranged alternately with, and very close to, the anodes. The $\overset{++}{\mathrm{Cu}}$ ions are attracted to the cathode, where they are discharged and deposited. An equal number of $\overset{++}{\mathrm{Cu}}$ ions are formed by the metal of the anode, passing into solution. The gold and silver have less tendency to ionize, so they drop to the bottom of the huge vat as a mud mixed with other impurities. Any zinc present in the anode would ionize more readily than the copper and would deposit on the cathode if the $\overset{++}{\mathrm{Cu}}$ ions were not so much more easily discharged. Very little difference of potential is needed, less than 0.5 volt. As measured in quantity of electricity Faraday's law shows that one equivalent weight of copper is deposited for every 96,540 coulombs of electricity. The value of the gold and silver recovered from the sludge is astonishing.

Properties of Copper. — Copper is red by reflected light, but greenish by transmitted light. The two colors may be observed with thin sheets such as ' Dutch foil." It melts at 1083° and boils at about 2300°. The melting point in air is lowered about 20° by the oxide formed, which is soluble in copper. The metal has a density of 8.93. It is remarkably malleable and ductile, and is the best electric conductor of the cheaper metals. If it lacked either in ductility or conductivity, there would not be much copper wire on the market.

Chemically copper is rather inactive. It is not oxidized in perfectly dry air, but in ordinary moist air a thin film of oxide forms. It does not decompose water, even boiling water, nor does it displace hydrogen from acids. However, oxidizing acids such as nitric attack it readily. This is due to the initial formation of copper oxide, which, like all metallic oxides, readily reacts with almost any acid.

Exercise 1. — What are the equations for the action of nitric acid on copper?

In parks we observe bronze statues covered with a green substance. This is basic cupric carbonate resulting from the combined action of oxygen, moisture and carbon dioxide on the copper of the bronze alloy. Although copper does not displace hydrogen from acids, almost any acid can attack it if in contact with air. Thus scrap copper wet with acetic acid in the air forms green basic copper acetate. The oxide forms first. At moderately elevated temperatures copper unites readily with sulfur and the halogens.

Uses of Copper. — The chief use of the metal is in the electrical industry for dynamos and motors as well as for wire to conduct the current. Second to this is its use in several important alloys such as brass bronze, German silver, bell metal, coinage and jewelry. Read again the discussion of Alloys on page 273. The earliest metal tools and weapons used by man were probably made of bronze because of its hardness and its ability to fill a mold sharply. Roofing, spouting and the sheathing of ships are sometimes made of copper.

Electroplating is important in book printing. A temporary set-up of type makes an impression in wax which is then brushed with graphite to make the surface an electrical conductor. The wax form is made the cathode in a bath of copper sulfate and coated with a thin layer of copper. After separation from the wax the thin copper shell is filled with lead to give it solidity. Such a type surface is permanent. Newspapers use less permanent material for their printing.

Compounds of Copper. — There are two series of copper compounds, cuprous and cupric, with valences of one and two. Cuprous salts are usually only sparingly soluble at most and are colorless. Many cupric salts are very soluble and all are blue in dilute solution. In other words the cuprous ion is colorless while the cupric ion is blue. At high temperatures cuprous compounds are more stable than cupric compounds. All copper salts are poisonous, yet small amounts were once used to "green" canned peas, pickles and other vegetables. This is prohibited now. Copper salts are especially poisonous to lower forms of life. For this reason carefully adjusted doses are sometimes added to water reservoirs to kill weed growth. All insoluble copper compounds except the extremely insoluble cupric sulfide are dissolved by alkali cyanides and by ammonium hydroxide.

Cuprous Oxide, Cu_2O. — This red oxide is found in nature as the mineral cuprite or ruby copper. In the laboratory it may be prepared by oxidizing copper at a gentle heat or by the addition of sodium hydroxide to a solution of cuprous chloride. Cuprous hydroxide is unknown, but it may possibly exist for an instant before losing water. The simplest way to prepare this oxide is to reduce *Fehling's solution* with glucose. This famous solution is a mixture of copper sulfate, sodium hydroxide and Rochelle salts (or any tartrate). A complex copper tartrate ion is formed which yields so few simple copper ions that no cupric hydroxide is precipitated. Yet enough cupric hydroxide is in solution to be reduced to cuprous oxide by added glucose. Since the occurrence of glucose in the urine is a symptom of diabetes, the use of Fehling's solution in diagnosis must be important.

Cuprous Chloride, CuCl. — This white, sparingly soluble salt is made only by reduction of cupric chloride. Boiling copper with cupric chloride in a solution of hydrochloric acid (absence of air prevents oxidation) is adequate to insure reduction:

$$CuCl_2 + Cu \rightarrow 2\ CuCl.$$

The hydrochloric acid is necessary to prevent hydrolysis of the cuprous chloride and precipitation of the oxide. This is a good example of mass action:

$$2\,CuCl+2\,H_2O \leftrightarrows 2\,HCl+Cu_2O+H_2O.$$

Concentrated hydrochloric acid has another influence. It reacts with cuprous chloride to form a soluble complex acid, $HCuCl_2$, which, on dilution, is decomposed with precipitation of cuprous chloride. It is worth stopping to inquire the ultimate explanation for the power of concentrated hydrochloric acid to dissolve cuprous chloride:

$$HCl+CuCl \rightarrow HCuCl_2.$$

The complex acid, $HCuCl_2$, yields $\overset{+}{H}$ ions and $\overset{-}{CuCl_2}$ ions. The latter ionize still further ($\overset{-}{CuCl_2} \leftrightarrows \overset{+}{Cu}+\overset{-}{Cl}+\overset{-}{Cl}$) but yield a smaller concentration of $\overset{+}{Cu}$ ions than is found in a saturated solution of cuprous chloride. Consequently all equilibria are disturbed in the direction that favors removal of cuprous ions from the solution:

$$CuCl \leftrightarrows \overset{+}{Cu}+\overset{-}{Cl},$$

$$\overset{-}{CuCl_2} \leftrightarrows \overset{+}{Cu}+\overset{-}{Cl}+\overset{-}{Cl}.$$

Specimens of cuprous chloride soon turn blue or green, due to oxidation. An ammoniacal solution of the chloride is very useful in analysis as an absorbent for carbon monoxide.

Cuprous bromide is easily made by heating the dry cupric salt ($2\,CuBr_2 \rightarrow 2\,CuBr+Br_2$). The iodide forms spontaneously from the cupric iodide:

$$2\,CuI_2 \rightarrow 2\,CuI+I_2.$$

It is possible to reduce cupric salts in solution with sulfur dioxide:

$$2\,CuSO_4+2\,H_2O+SO_2+2\,HCl \rightarrow 3\,H_2SO_4+2\,CuCl.$$

Cupric Oxide, CuO. — This black oxide is prepared by igniting copper powder in the air and by ignition of the nitrate and carbonate. Cupric hydroxide loses water slowly at room temperatures or quickly at 100°, with formation of the oxide. This occurs even when the hydroxide is immersed in water:

$$\begin{aligned}&2\ Cu+O_2 \rightarrow 2\ CuO,\\&2\ Cu(NO_3)_2 \rightarrow 2\ CuO+2\ NO+O_2,\\&CuCO_3 \rightarrow CuO+CO_2,\\&Cu(OH)_2 \rightarrow CuO+H_2O.\end{aligned}$$

If hot cupric oxide is reduced with hydrogen and then oxidized again in a stream of air, reduced again, oxidized again, and so on, it finally becomes so easy to reduce the oxide that a temperature of only 100° is sufficient. This is due wholly to the increase in surface.

Cupric Hydroxide. — This greenish-blue, gelatinous precipitate is formed by addition of a solution of any alkali to a solution of any copper salt:

$$CuSO_4+2\ NaOH \rightarrow Na_2SO_4+Cu(OH)_2.$$

EXERCISE 2. — Why isn't a precipitate of cupric hydroxide formed in Fehling's solution?

Cupric Sulfide, CuS. — This black sulfide is found in nature as the mineral covellite. It is the most insoluble copper salt we deal with in the laboratory. It can be precipitated from solutions of copper salts by hydrogen sulfide in spite of the presence of concentrated hydrochloric acid. Yet it is attacked by warm nitric acid with formation of the soluble cupric nitrate. The sulfur liberated is converted by continued oxidation into sulfuric acid.

Cupric Sulfate, $CuSO_4$. — This is the copper salt most used. It crystallizes in the rhombic system with five molecules of water as $CuSO_4.5\ H_2O$. At 120°–140° it loses four molecules of water, but must be heated to 240° before it loses the fifth molecule of water. The anhydrous salt is white and when crystallized from hot concentrated sulfuric acid exhibits a different crystal form from the "blue vitriol." The anhydrous powder is sometimes used as a dryer for alcohol and such liquids. As it takes up water it turns blue. The term "vitriol" was once applied to any sulfate, and sulfuric acid was termed "oil of vitriol." Ferrous sulfate was green vitriol and zinc sulfate was white vitriol.

Cupric sulfate is made by the action of hot concentrated sulfuric acid on scrap copper. Copper oxide is first formed and this easily reacts with acid:

$$Cu+H_2SO_4 \rightarrow CuO+H_2O+SO_2,$$
$$CuO+H_2SO_4 \rightarrow CuSO_4+H_2O.$$

On a large scale it is produced by roasting natural sulfides and leaching in the open air with water. Sometimes the copper ores are roasted and treated with sulfuric acid. Copper sulfate is used in calico printing, in electroplating, as a germicide, a fungicide and as a source of other copper compounds. Bordeaux mixture is made from copper sulfate and calcium hydroxide.

Other Copper Compounds. — The normal ***carbonate*** is not known. An attempt to precipitate it by union of the cupric ion and carbonate ion always results in a basic carbonate, because of hydrolysis:

$$2\ CuSO_4+2\ Na_2CO_3+H_2O \rightarrow Cu(OH)_2CO_3+2\ Na_2SO_4+CO_2.$$

The ***nitrate***, $Cu(NO_3)_2.6\ H_2O$, is a blue, soluble salt formed by the action of nitric acid on the metal, the oxide, the carbonate, or the hydroxide. (Equation?) The ***ferrocyanide***, $Cu_2Fe(CN)_6$, is a gelatinous, red precipitate formed by mixing solutions of copper sulfate and potassium ferrocyanide. It is the membrane used by Morse in his osmotic pressure work. Of course it had to be supported by a clay wall.

$$2\ CuSO_4+K_4Fe(CN)_6 \rightarrow 2\ K_2SO_4+Cu_2Fe(CN)_6.$$

A mixture of copper filings or powder with a solution of ammonium hydroxide and ammonium chloride absorbs an astonishing volume of oxygen. This is due to the primary formation of copper oxide and the conversion of this oxide into a soluble ammonia complex. Thus fresh copper surface is continually exposed to the oxygen.

Exercise 3. — Anhydrous cupric bromide, $CuBr_2$, is dark brown. With addition of very little water the color changes through brown to green and with more water to blue. In the light of the ionic theory, what explanation of this color change can you give?

Exercise 4. — Anhydrous cupric chloride is yellow. A concentrated solution is green and a dilute solution blue. Explain.

Ammonia Compounds. — Addition of ammonium hydroxide to a solution of copper sulfate, for example, first yields a green precipitate of basic cupric sulfate, $Cu_2(OH)_2SO_4$, and with an excess of ammonium hydroxide forms the beautiful rich azure-blue solution of the complex cupric ammonia sulfate, $Cu(NH_3)_4SO_4\text{-}H_2O$. This very soluble salt can be precipitated by addition of alcohol. A similar substance is secured by passing dry ammonia over anhydrous cupric sulfate. It releases ammonia on heating:

$$CuSO_4+6\ NH_3 \leftrightarrows Cu(NH_3)_6SO_4.$$

The soluble complex ionizes as follows:

$$Cu(NH_3)_4SO_4 \leftrightarrows \overset{+\ \ +}{Cu(NH_3)_4}+\overset{--}{SO_4}.$$

The $\overset{++}{Cu(NH_3)_4}$ ion yields such a low concentration of $\overset{++}{Cu}$ ions that many insoluble copper compounds are dissolved by ammonium hydroxide. Even cupric hydroxide is dissolved by ammonium hydroxide, with formation of $Cu(NH_3)_4(OH)_2$. The soluble salts form complex compounds as described for cupric sulfate. Cupric sulfide is the only copper compound not forming a soluble complex with ammonia.

Complex Cyanides. — Attempts to precipitate cupric cyanide fail. It decomposes spontaneously with escape of poisonous cyanogen gas, leaving a precipitate of cuprous cyanide:

$$CuSO_4+2\ KCN \rightarrow K_2SO_4+Cu(CN)_2,$$
$$2\ Cu(CN)_2 \rightarrow 2\ CuCN+(CN)_2.$$

With excess potassium cyanide the insoluble cuprous cyanide dissolves, forming potassium cuprocyanide:

$$CuCN+KCN \rightarrow K.Cu(CN)_2.$$

The complex negative $\overset{-}{Cu(CN)_2}$ ion $(K.Cu(CN)_2 \leftrightarrows \overset{+}{K}+\overset{-}{Cu(CN)_2})$ yields so few $\overset{+}{Cu}$ ions that all insoluble copper compounds are dissolved by alkali cyanides. Cupric sulfide is extremely insoluble. Its saturated solution (every precipitate settles from its own saturated solution) contains a minute concentration of $\overset{++}{Cu}$ ions, but the complex cyanides of copper yield a still smaller concentration of $\overset{++}{Cu}$ ions. Consequently addition of potassium or sodium cyanide to cupric sulfide disturbs every equilibrium in the direction favoring the existence of the lowest concentration of $\overset{++}{Cu}$ ions. It is worth remembering that most simple cyanides are insoluble but that all complex cyanides are soluble.

Tests for Copper Compounds. — Copper compounds (after moistening with hydrochloric acid to form the volatile chloride) burn with a green flame. Precipitation of the red cupriferrocyanide is a useful test. Usually the peculiar blue color developed when ammonium hydroxide is added to a solution of a copper compound is sufficient indication in analysis. Quantitatively the metal is commonly determined by electrolysis. The copper is plated on a weighed platinum cathode, dried and weighed.

Exercise 5. — Outline a chapter on copper and briefly discuss the important compounds. Arrange this logically and with the proper sense of proportion, just as if you were writing a book. This is the way to study every metal.

SILVER

Occurrence. — Silver is found free but generally alloyed with gold, copper or mercury. There are small deposits of horn-silver, $AgCl$, but the principal ore is argentite, Ag_2S, sometimes called silver glance. Lead and copper ores contain some silver which is recovered in the refining process. The United States, Canada and Mexico are all leading silver producers; in fact North America furnishes over 70 per cent of the world's silver, which usually totals about 170,000,000 oz. annually.

Metallurgy. — The *amalgamation process* is applicable to ores carrying free silver or to silver chloride. By roasting the sulfide ores with sodium chloride, they yield silver chloride, which can then be amalgamated. Crushed ores treated with mercury yield an amalgam of silver-mercury. This is separated from the waste rock and distilled in an iron retort. The volatile mercury is condensed for further use while the silver is left in the retort. Silver chloride with mercury yields metallic silver by simple displacement and the excess mercury then amalgamates it:

$$AgCl + Hg \rightarrow Ag + HgCl.$$

The *leaching process* may be applied to the sulfide ores. Silver sulfide is roasted to form the sulfate, which is dissolved by water.

Scrap copper added to the solution of silver sulfate displaces the silver and leaves copper sulfate as a valuable by-product:

$$Ag_2SO_4 + Cu \rightarrow 2\ Ag + CuSO_4.$$

Silver compounds are soluble in alkali cyanides, so ores may be leached with a solution of sodium cyanide. From this solution of the complex cyanide the silver is precipitated by zinc shavings.

The *Parkes process* of extracting silver from lead makes use of the principle involved in the extraction of fats from various mixtures by ether. Less than 2 per cent of zinc is melted with the lead. Since silver is far more soluble in zinc than in lead, it is nearly all taken up by the zinc layer floating on top. On cooling the zinc solidifies while the lead is still fluid. The zinc is removed and distilled off from the less volatile silver. On heating the silver in bone ash cupels any lead impurity is oxidized to lead oxide, which is taken up by the bone ash.

It should be noted here that most of our silver is a by-product of lead and copper refining.

Silver may be *refined* by heating in the air to convert other metallic impurities into oxides. It may be separated from gold, copper and iron by hot, concentrated sulfuric acid, which attacks all but gold. Scrap copper is added to the diluted solution to precipitate the silver:

$$Cu + Ag_2SO_4 \rightarrow 2\ Ag + CuSO_4.$$

A final purification by electrolysis in nitric acid solution, using the crude silver as anode, is possible.

Properties. — Silver is a white metal melting at 962° in absence of air. In the air it melts at 955°, due to the fact that 22 volumes of oxygen dissolve in one volume of molten silver, thus lowering the freezing point. On cooling, this oxygen escapes with a curious spattering of the surface crust. Silver is the best conductor of electricity and but for its cost would displace copper from the electrical industry. Silver is remarkably ductile, having been drawn to wire so fine that 1800 meters weighed 30 g. It is so malleable that foil has been prepared 0.00025 mm. in thickness. It boils at 1955° and has a density of 10.5.

Chemically, silver is inactive. It is not affected by hot oxygen, but is oxidized by ozone. It slowly reacts with sulfur and the halogens. Silver spoons become tarnished with a layer of the sulfide when in contact with eggs.

Uses of Silver. — Cheaper objects are electroplated with silver by making them the cathodes in a bath of the double cyanide. The plated surface has a frosted appearance until polished. Practically all mirrors are now made by reducing an ammoniacal solution of silver nitrate with glucose, formaldehyde, or Rochelle salts. The reduced silver is deposited on glass and is then varnished to protect it. In earlier days tin amalgam formed the reflecting surface. Silver is much used in coinage, ornaments, and in the preparation of its halogen salts for the photographic industry.

Silver Oxide. — The oxide is obtained as a brown precipitate ~~when a solution of any~~ alkali is added to a solution of a silver salt. It might be expected that silver hydroxide would be formed, but at least a part of this spontaneously loses water:

$$\begin{aligned} &AgNO_3 + NaOH \rightarrow NaNO_3 + AgOH, \\ &2\ AgOH \rightarrow H_2O + Ag_2O. \end{aligned}$$

A suspension of the oxide acts like a strong base, so it must be in equilibrium with some hydroxide in solution. The oxide is decomposed at 250° and is reduced by hydrogen at 100°. Ammonium hydroxide reacts with it to form the soluble complex, $Ag(NH_3)_2OH$. Compare with copper oxide.

Silver Halides. — These salts are usually formed by addition of a soluble halide to a solution of silver nitrate. The following table is of value in qualitative analysis.

SALT	COLOR	SOLUBILITY	EFFECT OF NH_4OH
AgI	Canary yellow	Most insoluble of the four	Insoluble
$AgBr$	Yellowish white	Insoluble	Soluble
$AgCl$	White	Insoluble	Soluble
Ag_2F_2	White	Soluble	— — —

The chloride and bromide both change in the light, hence their use in photography. Silver iodide is not changed by light unless an excess of silver nitrate be present. The chloride is fairly soluble in concentrated hydrochloric acid, due to the formation of the complex acid H_2AgCl_3. The $\overset{-}{AgCl_3}$ ion yields a lower concentration of $\overset{+}{Ag}$ ions than is found in a saturated solution of silver chloride. The iodide does not dissolve in ammonium hydroxide because in its saturated solution the concentration of $\overset{+}{Ag}$ ions is less than that in a solution of the silver ammonia complex ion. With the less insoluble bromide and iodide it is different. The action of ammonium hydroxide on silver compounds is quite similar to its action on copper compounds. The same may be said for the solvent action of potassium cyanide. Sodium thiosulfate dissolves the silver halides because of the formation of a stable complex ion, $\overset{-\ -\ -}{Ag(S_2O_3)_2}$:

$$AgCl + 2\ NH_4OH \rightarrow Ag(NH_3)_2Cl + 2\ H_2O,$$
$$AgCl + 2\ KCN \rightarrow KCl + K.Ag(CN)_2,$$
$$AgCl + 2\ Na_2S_2O_3 \rightarrow NaCl + Na_3Ag(S_2O_3)_2.$$

Photography. — The fundamental reaction in photography is that produced by the action of light on the silver halides:

$$4\ AgCl \rightarrow 2\ Ag_2Cl + Cl_2.$$

In the dark this reaction is slowly reversed. It is possible that one function of gelatin in sensitive films is to take care of the free chlorine or bromine. All chemists are not agreed on the existence of silver subchloride, Ag_2Cl, yet it may be formed. The sensitive film deposited on glass or celluloid is an emulsion (or, more accurately, a suspension) of silver halide in gelatin. (See chapter on Colloids.) By means of a lens an image is formed on the plate or film in the camera with varying intensities of light as reflected from white or darker objects. Thus the chemical effect of light on the silver halide varies throughout the film in accordance with the image. The image is said to be "latent" and is not visible to the eye until a developer (always a reducing solution) completes the reduction of the sub-halide to metallic silver. From the developing bath the plate is taken to a "hypo" bath of sodium thiosulfate, which dissolves any unused silver halide. If this were not washed out, later exposure to the light would render the entire image uniform. The washed and dried negative is then a picture composed of varying thicknesses of metallic silver. This is printed on sensitized paper, which is merely a film much like that of the original plate, backed by paper. Silver chloride papers yield a visible image without further treatment. These are used for "proofs." To make them permanent they are washed with sodium thiosulfate solution to remove unused silver chloride and are then "toned" in a solution of a gold or a platinum salt. Metallic silver displaces gold from solution, thus converting the image on the paper into the rich red-brown of metallic gold. Platinum prints, prepared in a similar way, are steel gray.

If silver bromide papers are used a latent image is obtained on printing. It is developed like the original plate. Since bromide papers are extremely sensitive, they are printed by artificial light.

Silver Nitrate. — Silver is dissolved by nitric acid with formation of the nitrate:

$$3\ Ag + 4\ HNO_3 \rightarrow 3\ AgNO_3 + NO + 2\ H_2O.$$

The white crystals of silver nitrate or "lunar caustic" are soluble in water. When pure the nitrate is not affected by light, but reducing agents readily cause formation of black metallic silver. When a solid stick of it is used to cauterize wounds, black stains develop by reduction. Its medicinal value may be due to precipitation of albuminoids.

Ammonium hydroxide is often added to silver nitrate solutions in order to secure the soluble complex ammonia compound. Only small quantities should be used, or if larger quantities are needed they should not be allowed to stand long. Several explosions have occurred, due to the probable formation of an unstable compound of silver and nitrogen.

EXERCISE 6. — How could you separate the silver from the copper in a silver coin?

Silver Cyanide, AgCN. — Addition of a soluble cyanide to a solution of a silver salt first precipitates the simple cyanide, AgCN. With excess of sodium cyanide, for example, the soluble complex, $Na.Ag(CN)_2$, forms. The concentration of simple $\overset{+}{Ag}$ ions in this solution is so very small that all insoluble silver salts (except the sulfide) are dissolved by alkali cyanides. A cyanide bath is often used in silver plating.

Other Silver Salts. — ***Silver sulfate, Ag_2SO_4,*** is white and moderately soluble. ***Silver carbonate, Ag_2CO_3,*** exists as a yellow salt, therefore silver hydroxide must be a moderately strong base or the carbonate would be completely hydrolyzed. ***Silver chromate, Ag_2CrO_4,*** is red and insoluble. The ***orthophosphate, Ag_3PO_4,*** is yellow and insoluble.

Tests for Silver. — The precipitation of white silver chloride, soluble in ammonium hydroxide without blackening, is usually considered a good test for silver compounds. Confirmatory tests may be obtained from the colors of the chromate and phosphate.

EXERCISE 7. — If silver and its compound suddenly ceased to exist, could we find adequate substitutes?

GOLD

Occurrence. — It is a good thing that gold is not a common metal. Otherwise our monetary standards would be sadly disturbed. We need a rare, inactive and beautiful metal of not too high a melting point for our standard coins. As it is, the gold production of the world has increased enormously in recent years, thus accounting for part of the increase in price of commodities.

Gold occurs free or alloyed with silver. Its only compound in nature is the telluride, AuTe. The United States produces one fifth of the world's gold, but the Transvaal of South Africa leads. Australia is third in the list. In 1910 the United States produced 4,657,018 oz., worth $96,269,100.

Metallurgy. — Since some gold is found in alluvial deposits, it may be separated by washing in a pan or sluice box. Gold, with its high density of 19.3, settles to the bottom, while the lighter sand, gravel, etc., with an average density of 2.6, is washed away. This is called "placer mining." Sometimes a powerful stream of water is used to force gold-bearing dirt into the sluices. This is "hydraulic mining."

Quartz rock carrying veins of gold is crushed and the material washed over cleats of amalgamated copper. The gold amalgam formed is worked up like the silver amalgam previously described. The tailings of waste rock carry considerable gold, which is leached out by means of sodium cyanide solution. (See metallurgy of silver.) The oxygen of the air is essential in this process:

$$4\,Au + O_2 + 2\,H_2O + 8\,NaCN \rightarrow 4\,NaAu(CN)_2 + 4\,NaOH.$$

Gold leaf placed in a bottle filled with boiled sodium cyanide solution does not dissolve, but if a stream of air be led through the solution the soluble sodium aurocyanide, $Na.Au(CN)_3$, is formed. Commercially the gold is finally secured by electrolysis or by displacement with zinc shavings. Successful reduction with zinc depends upon the partial removal of air:

$$2\,NaAu(CN)_2 + Zn \rightarrow Na_2Zn(CN)_4 + 2\,Au.$$

EXERCISE 8. — What is the similar reaction in winning silver?

Low-grade ores not worth mining before the introduction of the cyanide process in 1890 have been treated successfully in this way. In South Africa the cyanide method added enormously to the yield of gold, giving us a fine illustration of the relation of chemical reactions to economic conditions.

Properties. — Gold leads the metals in ductility and malleability. Gold leaf has been hammered so thin that it required 110,000 sheets to reach a total thickness of 1 cm. Gold wire has been drawn so fine that 3240 meters weighed only one gram. The element is yellow but the color can be varied by alloying it with silver and the other elements with it. Light transmitted through thin sheets is green. Gold melts at 1063° and volatilizes at temperatures not much higher. It is too soft to be used pure, so coins and jewelry contain copper as a hardening agent. United States gold coins are 90 per cent gold. In jewelry the purity of gold is rated by carats of fineness. Pure gold is 24 carats fine, while the usual jewelry alloy of 18 carats is only 18/24 pure. The specific gravity of pure gold is high, 19.3. Gold is readily obtained in colloidal suspensions that may be red, violet, blue or green, depending on the size of particle.

Chemically, gold is inactive. Not only is it indifferent to oxygen and hydrogen sulfide, but it resists the attack of nitric acid. However, free chlorine and bromine attack it. Consequently the mixture of concentrated nitric and hydrochloric acids called ***aqua regia*** dissolves gold, forming auric chloride, which, with excess of hydrochloric acid, forms chlorauric acid:

$$AuCl_3 + HCl \rightarrow H.AuCl_4.$$

Fused alkalies attack gold, forming aurates such as $NaAuO_2$.

Compounds of Gold. — There are two series of gold compounds, aurous and auric, in which it has the valence of one and three respectively. A starting point in the preparation of gold compounds is the ***chlorauric acid,*** $H.AuCl_4$, produced by the attack of aqua regia on the metal. The sodium salt of this acid, $NaAuCl_4 . 2\,H_2O$, is used in photography as a toner. On heating chlorauric acid the simple ***chloride,*** $AuCl_3$, forms. At higher temperatures (180°) ***aurous chloride,*** $AuCl$, is formed.

Auric hydroxide, $Au(OH)_3$, may be precipitated from sodium chloraurate by an alkali. If excess alkali be added, the hydroxide dissolves with formation of an aurate such as $Na.AuO_2.3\,H_2O$. Evidently the simple hydroxide is an acid capable of losing water before neutralization. ($Au(OH)_3 \rightarrow H_2O + H.AuO_2$.) Auric oxide, Au_2O_3, is brown, and aurous oxide, Au_2O, is violet.

In its chemical action gold is an acid-former, yet physically it is decidedly metallic.

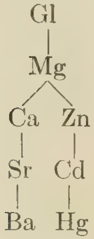
Tests for Gold. — The ease of reduction of gold salts to colored suspensions is of value in analysis. The Purple of Cassius, for example, is a characteristic color developed when a very dilute gold salt solution is warmed with a solution of stannous chloride containing a little stannic chloride. The color is due to a mixture of colloidal gold with colloidal stannic acid. The stannous chloride acted as a reducing agent. *Assaying* is interesting but not essential to first year work. An adequate discussion may be found in such books as Treadwell's *Qualitative Analysis*.

EXERCISE 9. — Review all the uses for sodium or potassium cyanide, both analytical and commercial.

CHAPTER XXXI

GLUCINUM, MAGNESIUM, ZINC, CADMIUM, MERCURY — Gl, Mg, Zn, Cd, Hg

GROUP II



The Group. — These elements do not form such a closely-knit family as barium, calcium, and strontium. Zinc and cadmium resemble each other in several respects, but mercury is so different that it is often studied in connection with copper. Glucinum and magnesium, as shown above, have some properties in common with the alkaline earths. All the elements of this group are bivalent, although mercury forms an additional series of compounds in which its valence is 1.

MAGNESIUM

Occurrence. — Magnesium compounds were discovered in 1695 when a spring at Epsom, England, was found to contain magnesium sulfate (hence the name, Epsom salts).

It is a very common element, although not a cheap metal, due to the cost of its preparation. It occurs as magnesite, $MgCO_3$, and as the double salt, dolomite, $MgCO_3.CaCO_3$. In the Stassfurt deposits it is found as the double chloride, carnallite, $KCl.MgCl_2.6\ H_2O$. Meerschaum is $Mg_2Si_3O_8.2\ H_2O$ and serpentine $Mg_3Si_2O_7.2\ H_2O$. Soapstone, or talc, is $Mg_3H_2(SiO_3)_4$ and asbestos, $CaMg_3(SiO_3)_4$.

Preparation. — Davy (1807) isolated the metal in impure form by electrolysis (compare sodium), but Liebig prepared a purer form in 1830 by reducing the chloride with metallic potassium. For a long time reduction with sodium was the commercial, but expensive, method of preparation. Now it is prepared by electrolysis of melted carnallite (melting point 700°), using carbon anodes and iron cathodes. Air is excluded by a stream of hydrogen.

Properties. — Magnesium is a silvery-white metal melting at 633° and boiling at 1000°. Its low density of 1.75 is interesting, for there is only one other commercial possibility, aluminum, among the light and strong metals to compete with it as an engineering material. It is important commercially that magnesium does not rust in dry air. A thin film of oxide, or probably basic carbonate, does form in moist air, but it is coherent enough to protect the metal beneath. Just below its melting point the metal can be drawn into wire. This wire is sometimes rolled into ribbon for special uses.

One of the chief uses of magnesium is in alloys with aluminum, one of which is called magnalium. These may contain from 10 to 25 per cent magnesium. They are harder, lighter, stronger and more easily machined than aluminum alone.

Chemically, magnesium is a rather active element, since it displaces hydrogen from boiling water. It also has some value in organic syntheses. Magnesium unites with most non-metals. With nitrogen it forms the nitride, Mg_3N_2, of interest because it reacts with water to form ammonia. Magnesium burns with a brilliant white light, strong in actinic rays, hence its use in flashlight powders. It was much used in star shells for military illumination. The fact that the metal burns in carbon dioxide shows that it is a powerful reducing agent when hot. It has been used to reduce silicon and boron from their oxides:

$$2\,Mg + CO_2 \rightarrow 2\,MgO + C,$$
$$SiO_2 + Mg \rightarrow 2\,MgO + Si.$$

Magnesium Oxide, MgO. — This white oxide is obtained by heating the carbonate ($MgCO_3 \rightarrow MgO + CO_2$). The reaction occurs at a lower temperature than that of a limekiln. Like calcium oxide, this oxide unites with water to form the hydroxide, but not with the evolution of as much heat. Its chief use is as a refractory lining for high-temperature furnaces. If the carbonate be used as a lining, it is turned into the oxide during use by the heat of the furnace.

Magnesium Hydroxide, $Mg(OH)_2$. — This compound is white and rather insoluble, so a suspension of it in water is used medicinally to neutralize undue acidity of the stomach and as a laxative. As fast as the small amount in solution reacts with acid more precipitate dissolves, so a small and harmless concentration of $\overset{-}{\mathrm{OH}}$ ions is maintained until all the precipitate is dissolved.

Magnesium Chloride, $MgCl_2$. — This salt is found in salt brines and is a by-product in separating potassium chloride from carnallite at Stassfurt. When heated sufficiently the crystallized salt, $MgCl_2.6\,H_2O$, is hydrolyzed completely by its own water of crystallization (favored by rise in temperature):

$$MgCl_2.6\,H_2O \rightarrow MgO + 5\,H_2O + 2\,HCl.$$

This reaction shows the danger from the use of sea water in boilers. The acid released attacks the metal of the boiler. When the Le Blanc soda process ceases to function it will be possible to make all the hydrochloric acid we need by heating crystallized magnesium chloride. The anhydrous salt can be prepared by heating carefully the double salt $MgCl_2.NH_4Cl.6\,H_2O$. The water is driven off first and then the ammonium chloride volatilized. The crystallized salt is used as a filler for cotton and woolen goods and in making magnesia cements. A wet mixture of the oxide and chloride hardens with formation of the basic chloride. Sawdust or wood meal is added as a filler. Such compounds make wall plasters or floorings. Of course any filler may be added.

Magnesium Carbonate, $MgCO_3$. — This salt occurs as the mineral magnesite in Greece, Austria, the United States and other countries. It was imported into this country, until the Great War, for furnace linings because the domestic product was unsuitable. When our importations were shut off our open-hearth steel furnaces and copper converters suffered. Finally it was proved that the foreign product had just enough iron oxide in it to give it the necessary wearing quality, while our own was too pure. Straightway enough iron oxide was mixed with Washington magnesite to give it the same quality. The deposits in Washington and California are extensive.

The normal carbonate cannot be obtained by precipitation with a solution of sodium carbonate. Instead, a basic salt is formed, its composition varying with the temperature and other conditions. The hydrolysis of sodium carbonate yields $\overset{-}{OH}$ ions as well as $\overset{--}{CO_3}$ and, since magnesium hydroxide is even more insoluble than the carbonate, the conditions favor formation of a basic salt such as $3\,MgCO_3.Mg(OH)_2.3\,H_2O$. This is sold as "magnesia alba" and used in cosmetics or in tooth powders. A crude product of loose fibrous structure is sold as "magnesia pipe covering" for heat insulation of steam pipes. In this field it is a rival to asbestos.

Magnesium Sulfate, $MgSO_4$. — There are deposits of magnesium sulfate in the western states and at Stassfurt. When crystallized from solution at ordinary temperatures the heptahydrate, $MgSO_4.7\,H_2O$, is secured. This is sold as Epsom salts. The various hydrates lose water at 200°. Magnesium sulfate is used in dyeing, tanning, as a filler for cotton goods and in medicine, paints, soaps and the laundry.

Magnesium Ammonium Phosphate, $MgNH_4PO_4$. — When any soluble orthophosphate is added to a solution of a magnesium salt with ammonium hydroxide and any ammonium salt a fine, crystalline precipitate of $MgNH_4PO_4$ is obtained. When ignited it forms the very stable pyrophosphate, $Mg_2P_2O_7$. This reaction is the basis of the quantitative determination of phosphates in fertilizers, etc.:

$$Na_2HPO_4+MgCl_2+NH_4OH \rightarrow 2\,NaCl+H_2O+MgNH_4PO_4.$$

A reagent called *magnesia mixture* is used in this precipitation. It might seem impossible to prepare a solution containing both $\overset{++}{Mg}$ ions and $\overset{-}{OH}$ ions (from $MgCl_2+NH_4OH$) and, in fact, if nothing else were added this mixture would form a precipitate of magnesium hydroxide. But the addition of any ammonium salt prevents precipitation. Ammonium hydroxide is a weak base and its ionization is greatly suppressed by the mass action of a great excess of $\overset{+}{NH_4}$ ions from the well-ionized ammonium chloride:

$$(1)\quad NH_4OH \leftrightarrows \overset{+}{NH_4}+\overset{-}{OH},$$

$$(2)\quad NH_4Cl \leftrightarrows \overset{+}{NH_4}+\overset{-}{Cl}.$$

The equilibrium in (1) is driven so far to the left that the concentration of $\overset{-}{OH}$ ions left is very small, too small with the $\overset{++}{Mg}$ ions present to exceed the solubility product of magnesium hydroxide. It is even possible to dissolve a precipitate of the hydroxide by addition of an ammonium salt. It is evident that the following equilibria must exist in a water suspension of magnesium hydroxide:

$$\text{Undissolved } Mg(OH)_2 \leftrightarrows \text{dissolved } Mg(OH)_2 \leftrightarrows \overset{++}{Mg} + \overset{-}{OH} + \overset{-}{OH}.$$

Removal of $\overset{-}{OH}$ ions, whether by addition of $\overset{+}{H}$ ions from an acid or $\overset{+}{NH_4}$ ions from ammonium chloride must disturb all equilibria continuously to the right, with final solution of the precipitate.

Tests. — The best test for magnesium compounds is the precipitation of the crystalline magnesium ammonium phosphate as described above.

EXERCISE 1. — In what localities do you expect to find the metal magnesium manufactured?

ZINC

Occurrence. — The world produces 880,000 tons of zinc annually and of this the United States accounts for 30 per cent. It is found in every state, although only twenty-three states are producers. The Missouri-Kansas-Oklahoma field leads, with lead sulfide-zinc sulfide ores. New Jersey is second with a unique mixture of oxides of zinc, iron and manganese called franklinite and a zinc silicate called willemite. Some zincite, the simple oxide, is found there. New Jersey boasts of the largest zinc mine in the world, producing 2000 tons of ore daily. Montana is next in order of importance, with the ores at Butte. Wisconsin, Colorado and Idaho are large producers. Sphalerite or zinc blende, ZnS, and smithsonite, $ZnCO_3$, are the chief ores in the western United States.

The ancients did not know zinc as a free metal, but produced brass by smelting zinc ores with copper. The Chinese isolated the element in the sixth century but Europe made no progress with it until the eighteenth century.

Metallurgy. — Many zinc ores need to be concentrated before smelting can be profitable, so the oil flotation process is used as with copper sulfide ores. Oxides or carbonates need only roasting with coal to reduce them to the metal. Sulfides must be roasted with excess air to secure the oxide of zinc, which is then further roasted with carbon to secure reduction. In some smelters a sulfuric acid plant is attached to utilize the sulfur dioxide:

$$2\,ZnS+3\,O_2 \rightarrow 2\,ZnO+2\,SO_2,$$
$$ZnO+C \rightarrow Zn+CO.$$

The zinc oxide and coal are heated in fire-clay retorts. The zinc is volatilized and then condensed in receiving vessels. Carbon monoxide burns at the mouth of each receiver. Since zinc boils at 925° and the temperature of the reduction is about 1200°, it is evident that the vapor of the metal must be formed. When the vapors are led into cold receivers at any temperature below 415° (melting point of zinc), only zinc dust is obtained, but as the hot vapors heat the receivers above 415° only the liquid form is condensed. This is cast into slabs called spelter. It may be purified by electrolysis (see Copper).

Properties of Zinc. — Zinc is a blue-white metal whose properties vary with its treatment. Cast zinc is hard and brittle, but if heated to 100°–150° it becomes so malleable that it can be rolled to thin sheets, which remain soft and malleable on cooling to ordinary temperatures. The density of cast zinc is 6.93 and of rolled zinc 7.18. The melting point is sometimes given as 415°, but varies above or below this according to the physical history of the sample. Zinc tarnishes in the air with formation of a film of basic carbonate. When very hot it reacts with steam:

$$Zn+H_2O \rightarrow ZnO+H_2.$$

It burns in air with a bluish flame and formation of white fumes of the oxide. It is the most active of the cheap metals, so it is made the "dissolving element" of most primary cells, yet pure zinc is scarcely attacked by dilute sulfuric acid. The presence of another metal or impurity, less active, causes a rapid attack of the zinc by the acid, although the bubbles of hydrogen are released on the surface of the other metal. Zinc dust particles are usually covered with a film of oxide. On exposure to moist air large quantities of zinc dust in storage have been known to take fire.

Uses of Zinc. — The most important use of the metal is in galvanizing iron to protect the iron from rusting. As zinc itself does not rust, the iron beneath cannot be attacked until the zinc surface is scratched or broken. Then with both metals in contact with moist carbon dioxide of the air we have a galvanic battery with solution of the more active metal, zinc. Later the iron is attacked. Galvanizing is done by cleaning the rust or scale from iron with dilute sulfuric acid and dipping the clean iron into melted zinc. On cooling the zinc crystallizes in the familiar spangled design. Another method of applying a zinc surface to iron is *sherardizing*. The iron wire or sheet is covered with zinc dust and baked at a temperature approaching 800°. The zinc penetrates the iron to some extent. By the *Shoop* process a spray of melted zinc is atomized with a blast of air or other gas. This spray of minute drops coats any object, wood, metal, paper, etc., with a coherent layer of zinc.

Rolled zinc is used for roofing, gutters, washing machine parts and battery elements. Alloyed with copper it forms brass, one of the most useful of all alloys. Zinc dust is a valuable reducing agent in organic syntheses. Zinc salts are poisonous, so food containers should not be made from this metal. Zinc shavings are used to displace gold and silver from the cyanide solutions employed in metallurgy.

Zinc Oxide, ZnO.—This white solid has been made by burning the metal, but most of it is prepared by direct roasting of the ores with a large excess of air. The dust is caught in bags which allow gases to go through. The oxide is yellow when hot, but pure white when cold. Artists use the best grade of it under the name, "Chinese white." Ground with linseed oil, it forms one of the best white paints. It is especially good for laboratories because hydrogen sulfide cannot change its color in forming white zinc sulfide. Painters now prefer an addition of from 5 to 35 per cent basic lead sulfate to zinc oxide in paints.

The greatest demand for zinc oxide, however, is as a filler in rubber goods, especially automobile tires. About 55 per cent of the weight of rubber tires is due to zinc oxide. It is mixed with gutta percha and Venice turpentine to make surgeon's adhesive tape. As a filler in oilcloth, celluloid and glazes it is important. Zinc oxide mixed with phosphoric acid sets quickly to a strong dental cement.

Zinc Hydroxide, $Zn(OH)_2$. — This white insoluble compound is readily formed by union of the $\overset{++}{\text{Zn}}$ ion of any soluble zinc salt with the $\overset{-}{\text{OH}}$ ions of any strong base:

$$\text{ZnSO}_4+2\ \text{NaOH} \rightarrow \text{Na}_2\text{SO}_4+\text{Zn(OH)}_2.$$

It is an *amphoteric* hydroxide acting like an acid and a base. It is dissolved by a strong acid which leads us to call it a base, but it is also dissolved by a strong base, so we are forced to call it an acid:

$$\text{Zn(OH)}_2+2\ \text{HCl} \rightarrow 2\ \text{H}_2\text{O}+\text{ZnCl}_2,$$
$$\text{Zn(OH)}_2+2\ \text{NaOH} \rightarrow 2\ \text{H}_2\text{O}+\text{Zn(ONa)}_2.$$

Sodium zincate, Zn(ONa)_2, is a soluble salt. Zinc hydroxide evidently forms both $\overset{+}{\text{H}}$ ions and $\overset{-}{\text{OH}}$ ions in water. The truth is some molecules ionize one way and some the other:

$$\text{Zn(OH)}_2 \leftrightarrows \overset{++}{\text{Zn}}+\overset{-}{\text{OH}}+\overset{-}{\text{OH}},$$
$$\text{Zn(OH)}_2 \leftrightarrows \overset{+}{\text{H}}+\overset{+}{\text{H}}+\overset{--}{\text{ZnO}}.$$

The student may ask here how it can ionize at all if it is insoluble. All compounds have some solubility, even if very minute in some instances. The very small amount of zinc hydroxide in solution is in equilibrium with its own ions and with the undissolved hydroxide:

$$\text{Undissolved Zn(OH)}_2 \leftrightarrows \text{dissolved Zn(OH)}_2 \begin{array}{l} \nearrow\!\!\swarrow\ \overset{++}{\text{Zn}}+\overset{-}{\text{OH}}+\overset{-}{\text{OH}} \\ \searrow\!\!\nwarrow\ \overset{+}{\text{H}}+\overset{+}{\text{H}}+\overset{--}{\text{ZnO}} \end{array}$$

When an excess of $\overset{+}{\text{H}}$ ions from a strong acid is added, the $\overset{-}{\text{OH}}$ ions are removed as water and every equilibrium disturbed in the direction of basic ionization. The entire precipitate is converted into zinc chloride or some such salt. On the other hand if an excess of $\overset{-}{\text{OH}}$ ions be added (strong base), the $\overset{+}{\text{H}}$ ions will be removed and every equilibrium disturbed in the direction of the acid ionization. All the precipitate is converted into some soluble salt such as sodium zincate.

Zinc hydroxide also dissolves in an excess of ammonium hydroxide, not because of the formation of ammonium zincate, but because of the formation of the soluble complex base, $Zn(NH_3)_4(OH)_2$. The concentration of simple $\overset{++}{\mathrm{Zn}}$ ions derived from further ionization of the $\overset{++}{\mathrm{Zn(NH_3)_4}}$ ion is lower than it is in a saturated solution of zinc hydroxide.

Exercise 2.— If ammonium zincate could be formed in any way, how would it react in aqueous solution? Why?

Zinc Chloride, $ZnCl_2$. — This very soluble salt can be made by the action of hydrochloric acid on the metal, the oxide or the carbonate. As a salt of a weak base and a strong acid, it is hydrolyzed, yielding an acid solution. It melts at 290° and on cooling forms a very solid mass. It has a strong affinity for water and is very caustic. It is much used as a timber preservative in railway ties and trestle work. It slowly digests cellulose to a soft gelatinous mass that may be molded into various shapes. After washing out the zinc chloride and drying we have fiber board, fiber buckets, etc., all light, strong and resilient. Pails must be varnished to make them waterproof. A wet mixture of zinc chloride and zinc oxide sets to a solid cement of the basic chloride. In this respect zinc resembles magnesium.

Zinc Sulfide, ZnS. — As the mineral sphalerite, zinc sulfide is yellow to black, but the pure precipitated compound is white (the only white sulfide). When roasted to a very moderate temperature it may be converted into the sulfate, but at higher temperatures it becomes the oxide. In the laboratory precipitation is secured by union of $\overset{++}{\mathrm{Zn}}$ ions and $\overset{--}{\mathrm{S}}$ ions. The sulfide ions may be from hydrogen sulfide or ammonium sulfide:

$$(1)\ ZnCl_2 + H_2S \leftrightarrows ZnS + 2\,HCl,$$

$$(2)\ ZnCl_2 + (NH_4)_2S \rightarrow ZnS + 2\,NH_4Cl.$$

In reaction (1) there is a serious difficulty. At first the concentration of $\overset{--}{\mathrm{S}}$ ions from the hydrogen sulfide may be sufficient, with the $\overset{++}{\mathrm{Zn}}$ ions, to exceed the solubility product of zinc sulfide.

$$[\overset{++}{\mathrm{Zn}}] \times [\overset{--}{\mathrm{S}}] = K, \text{ solubility product.}$$

But hydrochloric acid is formed as a by-product and its high concentration of $\overset{+}{H}$ ions greatly represses the slight ionization of hydrogen sulfide. Consequently very soon the $\overset{--}{S}$ ion concentration falls so low that the solubility product of zinc sulfide is no longer exceeded and no further precipitation occurs. To be sure, addition of some other ion that would remove the offending $\overset{+}{H}$ ions of the hydrochloric acid would permit precipitation. A strong base with its $\overset{-}{OH}$ ions could do this. So could sodium acetate, with its acetate ions which tie up most of the $\overset{+}{H}$ ions in the form of weakly ionized acetic acid:

$$\overset{+}{H}+\overset{-}{C_2H_3O_2} \leftrightarrows H.C_2H_3O_2.$$

Reaction (2) is favored because *salts* of hydrogen sulfide ionize freely and also because there is no acid formed to repress any essential ionization. So it is clear that zinc sulfide can be precipitated by passing hydrogen sulfide into a solution of any zinc salt containing sufficient sodium acetate or by use of any soluble sulfide other than hydrogen sulfide.

Lithopone. — This important pigment has been mentioned in connection with barium sulfide. It is made by mixing solutions of barium sulfide and zinc sulfate:

$$BaS+ZnSO_4 \rightarrow BaSO_4+ZnS.$$

Both products are white and insoluble. The precipitate first formed has no body or hiding power, but when washed, dried, heated to dull redness, suddenly quenched in cold water, ground wet, washed, and dried again, it yields an excellent pigment. Lithopone is a brilliant white with better hiding power than zinc oxide. It is unexcelled for interior painting, for first coats, floor oilcloth and several other uses. Curiously enough it darkens slightly in sunlight, but after a night's rest is as white as ever. This renewal is perpetual.

Tests. — The characteristic white color of zinc sulfide precipitated from solutions of zinc salts or zincates by ammonium sulfide is a test for it. Any zinc compound moistened with a solution of cobalt nitrate and heated on charcoal gives a green stain (Rinmann's green).

Exercise 3. — Why is zinc not used as a structural metal in the place of steel?

Zinc Chart:

- ZINC ORE
  - ZINC OXIDE
    - Paint
    - Pharmaceuticals
    - Rubber
      - Tires and Tubes
      - Rubber Foot Wear
      - Rubber Clothing
      - Surgical Rubber Goods
      - Mechanical Rubber Goods
    - Celluloid
    - Oilcloth
    - Printing Ink
    - Glue
    - Glass
    - Glazes
  - METALLIC ZINC
    - Rolled Zinc
      - Roofing
      - Gutters
      - Leaders
      - Weather Strips
      - Washing Machines
      - Boiler Plates
      - Battery Cells
    - Galvanizing
    - Brass
      - Apparatus and Instruments
      - Hardware
      - Sheets, Tubes and Rods
      - Lighting Fixtures
      - Castings
      - Bronzes
  - LITHOPONE
    - Linoleum
    - Flat Wall Paints
    - Window Shades

CADMIUM

Occurrence and Preparation. — Cadmium occurs in small quantities in zinc ores. Being more volatile than zinc it is found in the first distillate, from which it can be separated by fractional redistillation (in an atmosphere of hydrogen to prevent oxidation). Western zinc spelter carries about 0.4 per cent cadmium. It does some harm, but the cost of removal is discouraging.

Properties. — Cadmium looks much like zinc, melts at 321°, boils at 778° and has a density of 8.64. Its chief use is in low-melting alloys such as those used for automatic fire sprinklers and electric fuse wires. Some cadmium is also used for special solders and bearing metals.

Compounds. — The brown ***oxide, CdO,*** is formed by strongly heating the metal. It reacts with water to form the white insoluble ***hydroxide, $Cd(OH)_2$.*** This is not soluble in sodium hydroxide, so it is not amphoteric like zinc hydroxide. However, it dissolves in ammonium hydroxide, due to formation of the complex hydroxide, $Cd(NH_3)_4(OH)_2$. The soluble ***sulfate, $3\ CdSo_4.8\ H_2O$,*** is not strictly analogous to $MgSO_4.7\ H_2O$ nor to $ZnSO_4.7\ H_2O$.

Cadmium Sulfide, CdS, is its most important compound. It is a bright yellow and is used as a pigment under the name "cadmium yellow." The sulfide occurs as the mineral greenockite and is precipitated, even in weakly acid solutions, by union of $\overset{++}{\mathrm{Cd}}$ ions and $\overset{--}{\mathrm{S}}$ ions. However it dissolves in sufficiently strong acid, so it is best to precipitate in concentrations of acid not exceeding 0.5 N HCl.

The cadmium halides are but slightly ionized and in this respect the element resembles mercury (see page 149). An excess of alkali chlorides, bromides or iodides dissolves cadmium sulfide because the concentration of $\overset{++}{\mathrm{Cd}}$ ions in a halide solution is lower than in a saturated solution of the sulfide.

Tests. — The yellow color of cadmium sulfide is a distinctive test when separated from arsenic compounds. It differs from copper with which it is grouped in qualitative analysis in that the complex cadmocyanide yields enough $\overset{++}{\mathrm{Cd}}$ ions to allow precipitation of cadmium sulfide by hydrogen sulfide, while the similar complex cuprocyanide does not yield enough $\overset{++}{\mathrm{Cu}}$ ions to permit precipitation of the very insoluble copper sulfide.

Mercury

Occurrence and Metallurgy. — Because of the simplicity of its metallurgy, mercury has long been known. The alchemists were fascinated by its properties and attached great mysteries to it. To some extent it occurs free, but most of the world's mercury is obtained from the red sulfide, cinnabar, HgS. This is found in Spain, Austria, Italy, Mexico, the United States and Japan. Our domestic deposits are found in California and Texas, with a little in Oregon. Of the world's production of 3400 tons the United States produces about 700 tons.

The sulfide ore is roasted in air and the volatile mercury condensed. Any mercuric oxide formed would be decomposed at the roasting temperature:

$$\mathrm{HgS} + \mathrm{O_2} \rightarrow \mathrm{Hg} + \mathrm{SO_2}.$$

It is the commercial custom to sell the metal in iron flasks containing 75 pounds.

To purify the metal for accurate laboratory use it is usually allowed to fall in minute drops through a depth of two meters of dilute ferric chloride or nitric acid (density of 1.1) to oxidize any impurities. The nitric acid is contained in a long tube with the lower end drawn out and bent like a U. The bend of the U is kept filled with pure mercury, and any additional amount overflows into a receiver. To secure a spray of mercury a funnel is worked in the flame until a slight flange on the stem is formed and a bag of coarse canvas or chamois tied over this flange. In running through the cloth the metal is broken into many fine streams (Fig. 100).

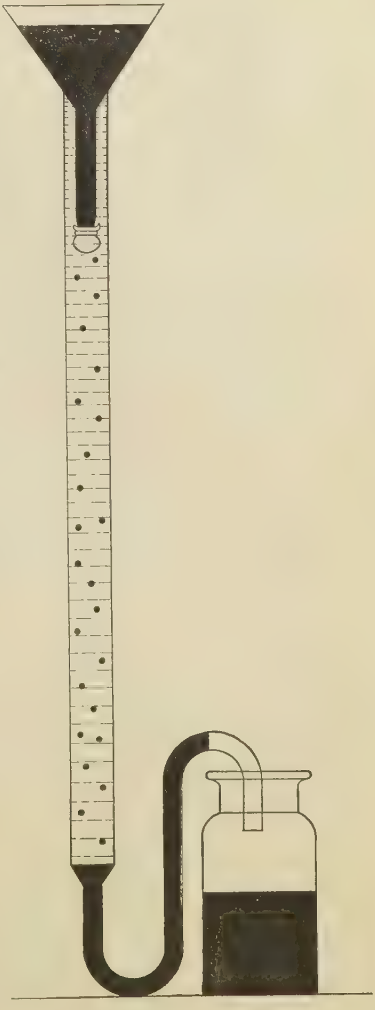


FIG. 100

Properties. — Mercury is a beautiful silvery liquid at ordinary temperatures; in fact it is the only metal liquid under such conditions. Cæsium comes near it. Mercury freezes at −39.4°, boils at 357° and has a high density 13.596 at 0°. It has a noticeable vapor tension at ordinary temperatures. A gold leaf suspended above the mercury in a bottle turns white eventually. When heated well above its boiling point, the vapor conducts electricity quite well, with radiation of a bluish-green light rich in ultraviolet rays. Lamps using this principle are made of glass tubes when only the visible light is desired, but when the ultraviolet rays are wanted for water sterilization, the tube must be of clear quartz. Glass stops ultraviolet rays, while quartz lets them through.

Mercury is used in thermometers, air pumps, gas measuring and collecting and was once essential to the manufacture of mirrors. Now all mirrors have a silver reflecting surface. Mercury forms amalgams with nearly all metals. It does not wet platinum or iron. The formation of amalgams with gold and silver is important in their metallurgy. Silver and gold amalgams are used in filling teeth. An amalgam of sodium and mercury (formed with the evolution of much heat) is useful as a reducing agent. The mercury dilutes the sodium, so the violence of its action on water is greatly lessened. Such an amalgam containing only 3 per cent of sodium is quite solid. Sodium and mercury form a definite series of compounds.

Chemically, mercury is almost a "noble" metal. It is oxidized slowly by air only above 300°, as Lavoisier learned in his classic experiment (page 13). However, it unites readily with sulfur and the halogens. Simple grinding of mercury and sulfur in the mortar produces some black mercuric sulfide. Mercury is not attacked by any acids except the oxidizing ones such as nitric and hot concentrated sulfuric acid. The metal is not poisonous in the mass, but all its soluble salts are, as is the vapor.

MERCUROUS COMPOUNDS

Mercurous Oxide, Hg_2O. — Addition of sodium hydroxide to a solution of any mercurous salt yields a black-brown precipitate of the oxide. This is very unstable in the light and on moderate heating:

$$Hg_2O \rightarrow Hg + HgO.$$

Mercurous Chloride, HgCl. — This insoluble white substance is used medicinally under the name *calomel*. It stimulates the liver and other glands. It is prepared by subliming mercury mixed with mercuric chloride:

$$HgCl_2 + Hg \leftrightarrows 2\ HgCl$$

This reaction is slightly reversible so the poisonous mercuric chloride must be washed out of the sublimate with alcohol or water. Medical men are careful to remember that light decomposes mercurous chloride ($2\ HgCl \rightarrow Hg + HgCl_2$) forming some of the extremely poisonous mercuric chloride. Consequently they always keep calomel in dark bottles. The white chloride blackens in contact with ammonia. The color is due to the finely divided metal:

$$2\ HgCl + 2\ NH_3 \rightarrow NH_4Cl + Hg + Hg(NH_2)Cl.$$

Mercurous Nitrate, $HgNO_3.H_2O$. — This is the most important soluble mercurous salt. It is obtained by the action of cold dilute nitric acid on excess mercury. Since mercury does not displace hydrogen from acids, the first step must be the formation of the oxide, which then reacts with the excess nitric acid. Mercurous nitrate is hydrolyzed to such an extent that some nitric acid must be added to prevent precipitation of the basic salt, $Hg_2(OH)NO_3$. Some free mercury must also be present to reduce any mercuric ions formed by an oxidation:

$$Hg + \overset{++}{Hg} \rightarrow 2\ \overset{+}{Hg}.$$

Mercurous Sulfate, Hg_2SO_4. — This white, slightly soluble salt is prepared in a manner analogous to that for mercurous nitrate. An excess of mercury is treated with sulfuric acid. Its chief use is in the standard cells for electrical measurements.

MERCURIC COMPOUNDS

Mercuric Oxide, HgO. — Lavoisier made this red substance by heating mercury in air at 300°–350°. This method is too slow, so usually it is prepared by heating dry mercuric nitrate with mercury. (See preparation of nitrogen dioxide.)

$$Hg(NO_3)_2 + Hg \rightarrow 2\ HgO + 2\ NO_2.$$

If sodium hydroxide be added to a mercuric salt solution, a yellow form of the oxide, HgO, is precipitated. The hydroxide has never been isolated. The yellow form is composed of smaller crystals than the red and is more active. As Priestley taught the world, mercuric oxide, heated to a temperature well above 350°, releases oxygen.

Mercuric Chloride, $HgCl_2$. — Mercury unites with chlorine with a green flame and production of mercuric chloride, but the usual method of preparation is to heat a mixture of mercuric sulfate and sodium chloride. A crystalline sublimate is secured:

$$HgSO_4 + 2\ NaCl \rightarrow HgCl_2 + Na_2SO_4.$$

A little manganese dioxide may be added before subliming in order to oxidize any mercurous sulfate formed. The sublimate melts at 288° and boils at 303°. It is somewhat soluble in cold water but much more so in hot water. Mercuric chloride forms more soluble complex salts with sodium or potassium chloride, such as $K_2HgCl_4.H_2O$. The simple salt is very poorly ionized, differing from the nitrate. In 0. 1 N solutions the chloride is only one per cent ionized and yields no precipitate with potassium dichromate. On the other hand mercuric nitrate in 0.1 N solution is 10 per cent ionized and yields a precipitate with this reagent.

This salt is extremely poisonous and is known to the public as *corrosive sublimate.* Since it coagulates albumen, the white of egg is the proper antidote.

Mercuric Iodide, HgI_2. — Mercuric iodide is formed as a yellow precipitate, instantly changing to scarlet, when $\overset{++}{Hg}$ ions and $\overset{-}{I}$ ions are brought together. When heated above 126° the red modification turns yellow. On cooling below 126° the yellow form may persist but on being scratched with some hard object it suddenly reverts to the red form. Similar color changes are found with some of the double iodides. With an excess of potassium iodide the soluble complex salt, $K_2.HgI_4$, is formed. Such a solution contains too low a concentration of simple $\overset{++}{Hg}$ ions to yield a precipitate of the oxide on addition of potassium hydroxide. Such a mixture of the complex salt and alkali is known as Nessler's solution. It is especially useful in analysis to detect and determine ammonium compounds. With ammonia a yellow color or even a precipitate is formed.

Mercuric Nitrate, $Hg(NO_3)_2$. — This is a colorless, soluble salt produced by dissolving mercury in an excess of hot nitric acid. (Compare with mercurous nitrate.) Its solution is very acid by hydrolysis.

Mercuric sulfate, $HgSO_4$. — By heating mercury in concentrated sulfuric acid mercuric sulfate is formed. It is soluble in dilute sulfuric acid, but in water is hydrolyzed to the yellow basic sulfate, $Hg_3(SO_4)O_2$. The sulfate and nitrate are more hydrolyzed than the chloride, because they are more ionized. ***Mercuric cyanide, $Hg(CN)_2$***, is more soluble than the chloride, but far less ionized; in fact it is the least ionized of all salts. Yet so insoluble is ***mercuric sulfide, HgS,*** that hydrogen sulfide precipitates it from the cyanide solution. It is a curious fact that precipitated mercuric sulfide is black, while the mineral cinnabar is red. However, on heating the black form in absence of air it sublimes as a dark red solid used as the pigment vermilion. It is not attacked by either concentrated hydrochloric acid or concentrated nitric, but the mixture of the two, aqua regia, converts it into the chloride and releases free sulfur. Nascent chlorine from any source will do the same thing.

Mercuric sulfide is dissolved by a solution of sodium sulfide:

$$HgS + Na_2S \rightarrow Hg(SNa)_2.$$

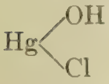
Since the compound formed is strongly hydrolyzed, it is necessary to add an excess of sodium hydroxide to prevent this. (Equations?)

Mercuric thiocyanate, $Hg(SCN)_2$, formed by mixing solutions of ammonium thiocyanate and mercuric chloride, is dried in pellets which are sold as "Pharaoh's serpents." When ignited these burn with startlingly voluminous ash twisted to resemble writhing serpents. ***Mercury fulminate,*** $Hg(ONC)_2$, is the usual detonating charge to set off high explosives.

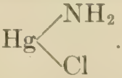
Complex Compounds with Ammonia. — E. C. Franklin, of Stanford University, has opened up a great field of work by studying reactions in liquid anhydrous ammonia. With mercuric salts three classes of compounds with ammonia are formed.

1. *Ammonia of crystallization.* Mercuric chloride, for example, unites directly with ammonia to form $HgCl_2.2\ NH_3$, much like $CaCl_2.8\ NH_3$.

2. *Ammono basic salts.* For instance, basic mercuric chloride,

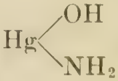


$Hg{<}\genfrac{}{}{0pt}{}{OH}{Cl}$, may be paralleled with



$Hg{<}\genfrac{}{}{0pt}{}{NH_2}{Cl}$.

3. *Mixed bases.* These may be represented by



$Hg{<}\genfrac{}{}{0pt}{}{OH}{NH_2}$ as a type.

In liquid ammonia the base comparable to KOH in water is the amide, KNH_2, which ionizes. ($KNH_2 \leftrightarrows \overset{+}{K} + \overset{-}{NH_2}$.) This "ammono base" reacts with acids (such as the organic acid amides) with formation of NH_3 (from $\overset{+}{H} + \overset{-}{NH_2}$) instead of H_2O as a neutralization product. Phenolphthalein shows a color change in this reaction just as it does in neutralization in a water system.

Tests for Mercury Compounds. — Precipitation of the white mercurous chloride which turns black with ammonia is the usual test for mercurous salts.

Mercuric salts are detected by formation of the black sulfide, which is then converted into mercuric chloride by aqua regia and reduced by stannous chloride:

$$2\ HgCl_2 + SnCl_2 \rightarrow 2\ HgCl + SnCl_4,$$
$$2\ HgCl + SnCl_2 \rightarrow 2\ Hg + SnCl_4.$$

At first the white calomel is precipitated and later this is completely reduced to the black finely divided mercury.

GLUCINUM

Glucinum, Gl, or beryllium, Be, as some people prefer to call it, occurs in the mineral beryl, a glucinum aluminum silicate. When this is transparent and tinted green with chromium silicate, it is called emerald. Wöhler prepared the element in 1828 by heating the chloride with potassium. It is a silvery white metal with a density of 1.9. It decomposes hot water slowly and reacts readily with dilute acids and dilute alkalies.

Glucinum hydroxide, $Gl(OH)_2$. — The hydroxide of glucinum is white, gelatinous and amphoteric, thus closely resembling zinc hydroxide. Its salts are strongly hydrolyzed. The name *glucinum* was given because of the sweetish taste of the soluble salts.

CHAPTER XXXII

ELECTROCHEMISTRY

Ionic Displacement. — Zinc dust, shaken with a solution of copper sulfate, removes the blue color with evolution of heat. After filtering, metallic copper is found on the filter and a solution of zinc sulfate in the filtrate. In other words, blue copper ions have become red copper molecules; and zinc molecules have become zinc ions. Equation (2) gives the essentials of equation (1):

$$(1)\quad \mathrm{Zn}+\overset{++}{\mathrm{Cu}}+\overset{--}{\mathrm{SO_4}}\rightarrow \mathrm{Cu}+\overset{++}{\mathrm{Zn}}+\overset{--}{\mathrm{SO_4}},$$

$$(2)\quad \mathrm{Zn}+\overset{++}{\mathrm{Cu}}\rightarrow \mathrm{Cu}+\overset{++}{\mathrm{Zn}}.$$

Apparently, the zinc atom is better able to take or hold positive charges than is the copper atom. In reality the zinc atom in gaining two positive charges has given away two electrons (negative charges of electricity) to the copper ion. Loss of electrons by a metallic atom means the formation of a positive ion. A number of other displacement reactions have already been observed by the student. The displacement of hydrogen from acids is especially familiar:

$$\mathrm{Zn}+2\,\overset{+}{\mathrm{H}}\rightarrow \overset{++}{\mathrm{Zn}}+\mathrm{H_2},$$

$$\mathrm{Zn}+2\,\overset{+}{\mathrm{Ag}}\rightarrow \overset{++}{\mathrm{Zn}}+2\,\mathrm{Ag},$$

$$\mathrm{Fe}+\overset{++}{\mathrm{Cu}}\rightarrow \overset{++}{\mathrm{Fe}}+\mathrm{Cu}.$$

Evidently a displacement series of the metals can be arranged in which a given metal will displace from salt solutions any metal below it, but will in turn be displaced by any metal above it. Such a series has a number of names. It was given on page 57 as the "activity series" with the most active metals at the top. Now we see that those at the top have the greatest tendency to lose electrons — to go into solution as ions. Hence the name, "solution tension series." For reasons to be made clear later, it is also called the "electromotive series." An abbreviated list of the metals in proper order follows:

Most active
K
Na
Li
Ba
Ca
Mg
Al
Fe
Ni
Sn
Pb
H
Cu
Ag
Au
Pt
Least active

Electric Cells. — When a strip of zinc is placed in a solution of copper sulfate all the energy of the reaction is evolved as heat (Fig. 101). There is no current of electricity, that is, no flow of electrons along a wire or other circuit. The copper ions come in direct contact with the metallic zinc. However, if they are kept apart by a suitable device the same reaction may take place but with the important difference that all the energy is released as electricity. Solutions of zinc sulfate and copper sulfate may be kept apart by a porous clay wall which permits ions to wander through when attracted but hinders ordinary diffusion (Fig. 102). A zinc plate is placed in the zinc sulfate compartment and a copper plate in the copper sulfate compartment. On connecting the two plates by a wire a current of positive electricity flows along the wire from copper to zinc and through the solutions to the copper. This device is a primary cell

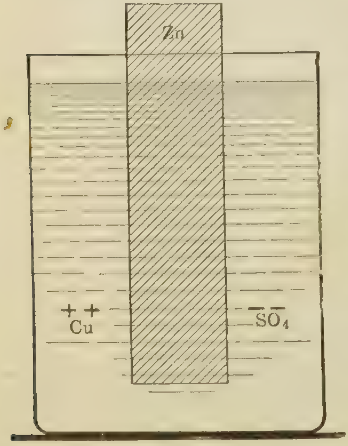


Fig. 101

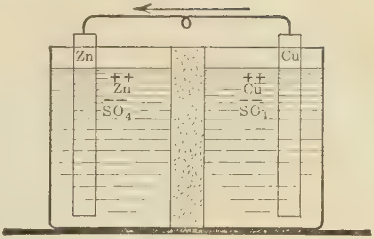


FIG. 102

(as differing from a secondary or storage cell) and converts chemical energy into electrical energy. The zinc, with a greater solution tension, or pressure, than the copper, throws atoms into solution as ions. This means that some zinc atoms give up electrons to the rest of the zinc plate. These electrons flow along the wire (current of negative electricity) to the copper plate, where they are readily taken up by the adjoining copper ions. This action neutralizes the charge on the copper ions and causes a deposition of metallic copper on the plate. The zinc plate is finally dissolved and the copper ions all removed. The excess $\overset{++}{Zn}$ ions attract $\overset{--}{SO_4}$ from the other compartment, so all portions of the solutions are kept electrically neutral.

Many such cells are possible. In fact, any two metals in a solution of any electrolyte may be connected as a cell somewhat similar in action to the one just described. In all cases the more active metal dissolves. The direction of the current, as arbitrarily named, is opposite to the flow of electrons along the wire. This decision as to the direction of flow was made before scientists knew anything about electrons.

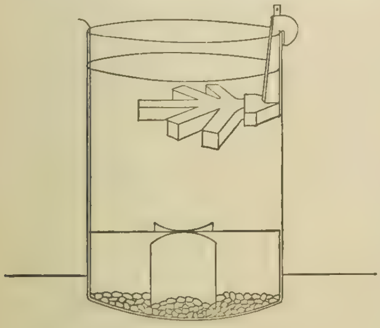


FIG. 103

The Gravity Cell (Fig. 103) is a convenient arrangement of the zinc-copper cell. The copper plate lies in a saturated solution of copper sulfate, while the zinc plate (shaped like a crowfoot) is hung over the edge of the jar in the lighter solution of zinc sulfate or dilute sulfuric acid. Thus gravity helps to keep the two solutions apart without a diaphragm. This battery, in either form, is often called the Daniell cell.

Electromotive Force. — The force that drives the electrons along a metallic circuit is termed *electromotive force* (E.M.F.)

or voltage and its unit of measurement is the volt. The difference in this pressure or potential between the two poles of a Daniell cell is 1.10 volts. Other cells, such as the Clark and Weston, are better standards. If a cell is made of two metals close together in the electromotive series, the voltage is very low. The farther apart they are in the series the higher the voltage.

Solution Pressure. — Any metal in water has a slight tendency to throw atoms into solution as ions (Fig. 104). There is an actual solution pressure differing in degree with different metals. Since the rest of the metal becomes negative, the positive ions are attracted back to the metal and exert an osmotic pressure opposing the solution pressure. Of course the osmotic pressure equals the solution tension in most cases when there are but few ions present. The reaction is reversible:

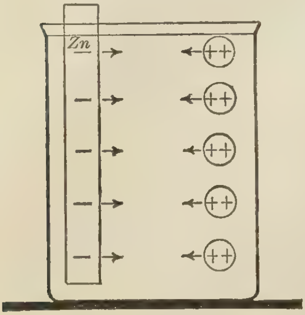


FIG. 104

$$Zn \leftrightarrows \overset{++}{Zn}.$$

However, when a wire connects this metal with another strip of a less active metal in the solution the negative charge flows through the wire to the other pole and there discharges some positive ions. This action leaves the layer of attracted positive ions around the first metal free to diffuse away, and thus more ions can form from the more active metal. This is battery action.

If a metal strip be placed in a solution of one of its own salts, its solution pressure is opposed by an osmotic pressure varying with the concentration. The potential difference, then, between a metal and such a solution depends somewhat on the concentration of the solution. It is customary to compare potentials in normal solution. Such a table follows:

POTENTIAL IN VOLTS, OF ELEMENTS IN NORMAL SOLUTIONS OF THEIR SALTS. (ELECTROMOTIVE SERIES.) (FROM WASHBURN.)

Li	−3.03	Zn	−0.76	Ni	−0.2	Cu(++)	+0.34
K	−2.93	Fe(++)	−0.43	Pb	−0.12	Hg	+0.80
Na	−2.72	Cd	−0.40	Sn	−1.10	Ag	+0.80
Mg	−1.55	Co	−0.3	H	+0.0	Au	+1.5

(It is to be noted that this table gives the sign of the metal strip placed in the solution. Some other tables use the sign of the solution itself which is opposite. There need be no confusion.)

From this table the voltage of any combination may be calculated. It is merely the difference in potential between the two elements. For example, the voltage of the Daniell cell (Cu−Zn) is $+0.34-(-0.76)=1.10$ volts.

Exercise 1. — What is the voltage of the Pb-Pt cell?

It is interesting to learn that the voltage of a Daniell cell can be radically changed by adding ammonia to reduce the concentration of $\overset{++}{\mathrm{Cu}}$ ions. Potassium cyanide reduces the concentration so much that the copper plate actually goes into solution (solution tension exceeds osmotic pressure) and the action of the cell is reversed. Zinc is deposited.

Electric Energy. — Electric energy is measured by the product of the intensity factor times the quantity factor. The volt is the unit of intensity and the coulomb the unit of quantity. Since the flow of water in a pipe leading from an elevated reservoir is somewhat comparable to the flow of electricity, we may consider the difference in electric potential between any two points in a circuit as analogous to the difference in "head" or pressure of water at the reservoir and at the open tap. The unit of actual quantity of water is the gallon, no matter what the pressure or rate of flow. The coulomb is likewise a unit of actual quantity of electricity. A gallon of water delivered under a definite pressure delivers a definite amount of energy to a water motor. So a coulomb of electricity delivered under a certain voltage or electrical pressure delivers a definite number of joules of energy:

$$1 \text{ volt} \times 1 \text{ coulomb} = 1 \text{ joule}$$

$$1 \text{ joule} = 0.24 \text{ cal.}$$

A simple definition of the coulomb may be taken from the fact that 96,540 coulombs of electricity will discharge one gram-equivalent weight of any ion during electrolysis. When one gram-equivalent weight of zinc displaces copper from a solution of a copper salt, 25,050 cal. of heat are liberated.

Exercise 2. — Calculate how many coulombs are delivered in a Daniell cell when one gram-equivalent weight of zinc is dissolved. Give the heat equivalent of the electrical energy evolved.

The *rate* of delivery of a given number of joules is important. One coulomb per second means a current strength of one ***ampere*** (similar to one gallon of water per second). The unit of rate of delivery is the ***watt:***

$$1 \text{ ampere} \times 1 \text{ volt} = 1 \text{ joule per sec.} = 1 \text{ watt.}$$

The horsepower is 746 watts (about as much energy as a common electric iron uses). A 40-watt lamp on a 110-volt circuit must use a 0.36 ampere current:

$$x \text{ amperes} \times 110 \text{ volts} = 40 \text{ watts,}$$
$$x = 0.36 \text{ ampere.}$$

Electric energy is sold by the kilowatt (1000 watts) hour.

Oxidation and Reduction. — Loss of electrons from a metallic atom or ion is oxidation, while gain of electrons is reduction. The zinc atom is oxidized in becoming the zinc ion and the $\overset{++}{\text{Fe}}$ ion is oxidized in becoming the $\overset{+++}{\text{Fe}}$ ion. In the Daniell cell the general effect is the oxidation of zinc atoms by $\overset{++}{\text{Cu}}$ ions. When this oxidation and reduction occur at the same point heat is evolved, but when they occur at two different points, as in an electric cell, the energy appears as a current of electricity.

This oxidation and reduction can be demonstrated clearly by the use of a salt bridge (Fig. 105). In one beaker is a solution of ferrous chloride and in the other a solution of sodium chloride and chlorine. An inverted U-tube filled with sodium chloride solution

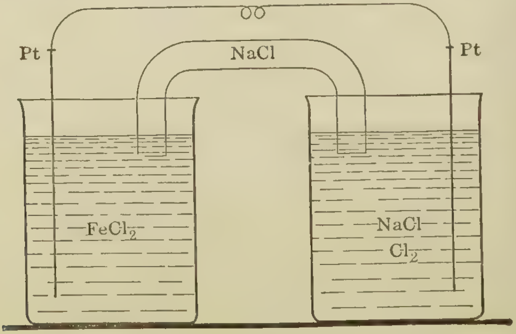


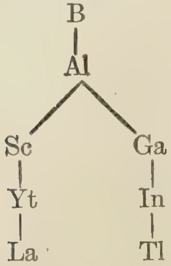
Fig. 105

connects the two beakers. The platinum poles are connected by a wire. The $\overset{++}{\mathrm{Fe}}$ ions give one electron to the platinum pole, thus becoming $\overset{+++}{\mathrm{Fe}}$ ions. These electrons flow along the wire to the platinum pole in the other beaker, where they are taken up by chlorine atoms. These $\overset{-}{\mathrm{Cl}}$ ions then travel through the U-tube, attracted by the excess of positive changes of the $\overset{+++}{\mathrm{Fe}}$ ions. Thus ferrous chloride is oxidized by chlorine, which never comes in contact with the iron salt.

CHAPTER XXXIII

ALUMINUM AND THE RARE EARTHS

The Group



Of the elements of the trivalent group only the first two are common — boron and aluminum. Of the remainder, it need only be said that their salts are extremely rare — scandium, the existence of which was predicted by Mendeleef a few years before the element was discovered, yttrium and lanthanum as one subgroup; and gallium, indium and thalium as the other. Boron has already been studied in connection with silicon because its hydroxide is a weak acid. Aluminum hydroxide is both acid and basic, in fact the element is more metallic than boron. The elements on the left of this column in the periodic table are somewhat more basic than the others of the group, hence their salts are not so readily hydrolyzed.

Within this group, as within all other groups of the periodic table, basic properties of elements increase with increasing atomic weight.

Aluminum

Occurrence. — Aluminum is the most extensively distributed of the metals. It never occurs free, but nearly all rocks except sandstone and limestone contain aluminum compounds. Such silicates as feldspar, $KAlSi_3O_8$, and mica, $KAlSiO_4$, are common.

Ordinary clay, $H_2Al_2(SiO_4)_2.2\ H_2O$, cryolite, Na_3AlF_6, bauxite, $Al_2O_3.2\ H_2O$, and corundum, Al_2O_3, are well-known compounds of aluminum.

Preparation. — Aluminum was the latest of the great commercial metals to come into use. This was due largely to the difficulty of reduction of its oxide. Wöhler was the first to produce it (1827). He heated the anhydrous chloride with metallic potassium:

$$AlCl_3 + 3\ K \rightarrow Al + 3\ KCl.$$

This method, yielding a metal that sold for $160 per pound, was not destined to make aluminum compete with anything but museum specimens. The French chemist, Deville, improved the process in 1856 by using the cheaper sodium instead of potassium and the less volatile double chloride of sodium and aluminum instead of the simple chloride. The price fell to $15 per pound. Castner, the American, attempted to cheapen aluminum by cheapening sodium and in this he succeeded in 1886. His work forced aluminum down to $4 per pound. A large sodium plant was erected for the new industry, but just then Castner's plans were upset by Hall's wonderful discovery in 1886. Nothing daunted, Castner went ahead and invented the highly successful Castner cell for producing sodium hydroxide by electrolysis of sodium chloride.

Charles M. Hall, a student in Oberlin College, attacked the problem of making cheap aluminum and succeeded where the greatest scientists of the century had failed. It occurred to him that if he could find an easily melted mineral in which aluminum oxide dissolved, the solution might be electrolyzed. Such a rock he found in cryolite, $3\ NaF.AlF_3$, from Greenland. Hall secured his electric current from all the batteries he could borrow or make. By melting the cryolite in a graphite crucible with the heat of a gasoline torch and using a carbon anode he managed to secure a few globules of the precious metal. Within six months after his graduation in 1886 this youth of twenty-two years laid the foundation for a great industry. It is interesting to know that a few months later the young Frenchman, Heroult, duplicated Hall's discovery quite independently. Hall had the usual inventor's troubles in getting a market for his ideas, but by 1889 his company was producing aluminum commercially (Fig. 106). The price fell to 18 cents per pound in 1914, but of course rose somewhat during the war. The production had grown rapidly but the Great War stimulated the demand beyond all previous records. In 1918 the world used about 500,000,000 pounds and the United States produced almost half of this great total. Hall's original company is still the sole producer in this country, not because of patents, for they have expired, but because of possession of the best ore deposits and perfection of manufacturing operations. The best bauxite deposits in the world were supposed to be in France but the American company has recently secured control of a vast deposit in British Guiana that is purer than French ore. Previously the supply was secured from Arkansas, Georgia, Tennessee and Alabama.

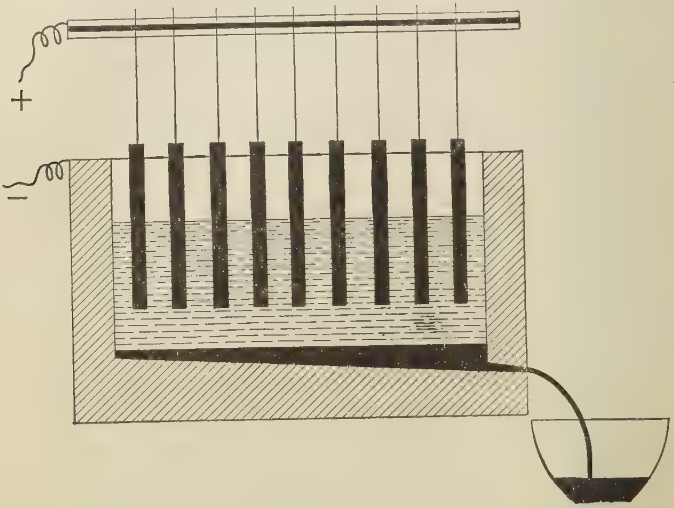


Fig. 106

Most bauxite contains iron oxide as an impurity. This is removed by digesting the ore with concentrated sodium hydroxide under steam pressure which dissolves the aluminum as sodium aluminate but does not attract the iron oxide. This solution is then treated with freshly precipitated aluminum hydroxide which precipitates the greater portion of the aluminum from the solution in the form of aluminum hydroxide.

The caustic filtrate is used to digest more bauxite. The ignited hydroxide (now alumina, Al_2O_3) is added to the cell ready for electrolysis. These cells are iron boxes lined with a tarry material. About 40 carbon anodes dip into the bath, which is kept molten (at 900°–1000°) merely by the heat of resistance. The iron cell is the cathode. The metal is discharged at the cathode and sinks to the bottom, to be tapped off from time to time. Oxygen is evolved at the anodes. Since it is only the dissolved alumina that is decomposed the cryolite should never need renewal — but it does. Calcium fluoride and other materials are now added to improve the bath. The potential fall in a cell is only about 5 volts, but a flow of several thousand amperes is maintained.

Properties. — The metal aluminum is the lightest of all the common metals, its density being only 2.6 while iron is three times as heavy. In color it somewhat resembles silver but with a bluish light. It melts at 658° and boils at 1800°. It is rolled or hammered most easily at 100°–150°. Near the melting point it is so brittle that it can be ground to a powder. It is an excellent conductor of heat and electricity. In wire of the same cross section it conducts electricity only two thirds as well as copper, but weight for weight it excels copper in this respect. Only iron and copper have greater tensile strength.

Chemically aluminum is very active, yet it is tarnished only slightly in air. This is due to the formation of a thin coherent film of the oxide which protects the metal beneath. Hydrochloric acid dissolves it readily with escape of hydrogen, but dilute nitric acid attacks it slowly. This is probably due to the oxidizing action of nitric acid. When aluminum is wet with a dilute solution of mercuric chloride, mercury is displaced (why?) and at once forms an amalgam with the aluminum. This amalgamated aluminum rapidly displaces hydrogen from water while the insoluble hydroxide forms. Like zinc this metal is dissolved by solutions of sodium or potassium hydroxide:

$$2\ Al + 6\ NaOH \rightarrow 2\ Al(ONa)_3 + 3\ H_2.$$

Uses of Aluminum. — Because it is light, strong and not noticeably corroded in air aluminum has many commercial uses. A leading metallurgist predicts that in half a century it will rank second to iron among the metals in annual tonnage. It is now used in large quantities to remove air bubbles from steel ingots at the moment of pouring. The light aluminum oxide formed floats to the top. Aluminum is much used for auto parts, the rigid structure of airships and structural work of various kinds. The powdered metal is mixed with oil or a volatile liquid and used as a paint for radiators and other metallic articles. In the form of cooking utensils it has a merited popularity. Since its salts are not poisonous the thin foil is coming into use as a food wrapper. The alloy with magnesium, called magnalium, is stronger and is machined more readily than aluminum itself. Aluminum cannot be turned easily in a lathe. Aluminum bronzes formerly contained 90 per cent copper and 10 per cent aluminum, but now these proportions are varied widely and small percentages of other elements added. Some modern alloys of this type contain more aluminum than copper. They have the advantage of strength approaching that of steel, great hardness, resistance to corrosion, beauty, susceptibility to high polish and lightness. Finally, such a bronze can be cast while steel cannot. In all probability the greatest future of aluminum lies in the direction of alloy making.

"Aluminothermy" is a process developed by Goldschmidt, who discovered that powdered aluminum when ignited reduces many metallic oxides with evolution of a great amount of heat (Fig. 107). Temperatures of 3000° are obtained so the molten metal may be cast in a mold:

$$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe.$$

If a shaft on a ship at sea had been broken the ends could be welded together by surrounding them with a sand or clay mold and igniting a mixture of iron oxide and aluminum powder (thermit) in a funnel above. The melted iron runs into the mold, melts the broken ends of the shaft and produces a perfect union. In actual practice the shaft ends are preheated.

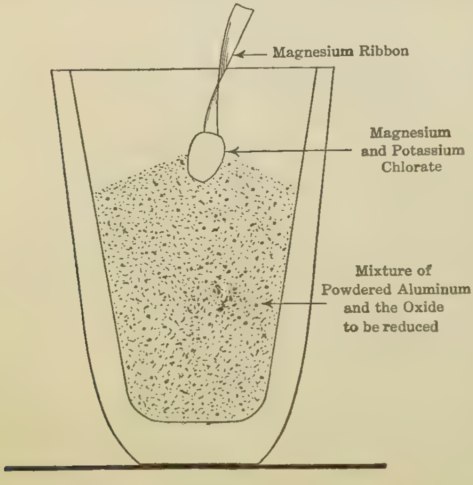

Magnesium Ribbon
Magnesium and Potassium Chlorate
Mixture of Powdered Aluminum and the Oxide to be reduced

FIG. 107

Aluminum Oxide, Al_2O_3. — The mineral bauxite may be considered as the partly dehydrated hydroxide or the hydrated oxide. Corundum is an impure form of the oxide, extremely hard, hence the variety known as emery is used as an abrasive or polishing material. Emery contains some iron oxide. The mineral bauxite is heated until portions fuse and then ground to a powder. This is really artificial corundum and is used as an abrasive under the name alundum. The gems, ruby and sapphire, are crystals of pure corundum colored by traces of other metallic oxides.

Artificial Gems. — Artificial rubies and sapphires are now manufactured that are in every way the equal of the natural gems, chemically and artistically. When powdered ammonium alum, $NH_4Al(SO_4)_2.12H_2O$, is sifted through an oxyhydrogen flame it melts. The drops are caught on a very small support and finally build up a "boule" of Al_2O_3 in the shape of an inverted chestnut. Ammonia and sulfur trioxide are volatilized with the water of the alum. This boule looks like a clear glass but in reality it has a crystalline structure. It is cut and polished, yielding beautiful "white sapphires." If a trace of chrome alum, $NH_4Cr(SO_4)_2.12\ H_2O$, is crystallized with the other alum, the chromium oxide formed as an impurity changes the white sapphire to a magnificent ruby. This may be pink or deep red, depending on the amount of chromium oxide present. A pigeon blood ruby worth several hundred dollars can be duplicated for a few dollars. Yet not exactly duplicated, for under the microscope the minute bubbles in the artificial ruby are found to be rounded, while those in the natural gem are flat sided. The blue color of sapphires is obtained by the use of a trace of titanium oxide.

Wade's interesting little book, *Precious Stones* (Putnam and Sons), is worth reading.

Aluminum Hydroxide, $Al(OH)_3$. — This white, insoluble hydroxide is precipitated when any soluble base is added to a solution of an aluminum salt; in other words, by the union of $\overset{+++}{\text{Al}}$ ions with $\overset{-}{\text{OH}}$ ions:

$$AlCl_3 + 3\ NaOH \rightarrow Al(OH)_3 + 3\ NaCl.$$

That it is a basic hydroxide is clearly shown by the fact that many acids dissolve it:

$$Al(OH)_3 + 3\ HCl \rightarrow AlCl_3 + 3\ H_2O.$$

That it is an acid is just as clearly shown by the startling fact that sodium and potassium hydroxides dissolve it:

$$Al(OH)_3 + 3\ NaOH \rightarrow Al(ONa)_3 + 3\ H_2O.$$

There is but one explanation. Aluminum hydroxide is amphoteric, some molecules ionizing as an acid and some as a base. If the objection be raised that this hydroxide is insoluble, it can be pointed out that a very small amount is really in solution, and in equilibrium with the undissolved phase:

$$\text{Undissolved Al(OH)}_3 \rightleftarrows \text{dissolved Al(OH)}_3 \begin{array}{l} \rightleftarrows \overset{+++}{\text{Al}} + \overset{-}{\text{OH}} + \overset{-}{\text{OH}} + \overset{-}{\text{OH}} \\ \rightleftarrows \overset{+}{\text{H}} + \overset{+}{\text{H}} + \overset{+}{\text{H}} + \overset{---}{\text{AlO}_3} \end{array}$$

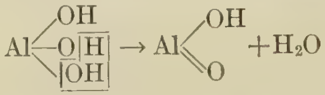
These equilibria may be disturbed in one direction by addition of an excess of $\overset{-}{\text{OH}}$ ions or in another direction by addition of an excess of $\overset{+}{\text{H}}$ ions. (Compare with zinc hydroxide.)

With weak bases or weak acids, aluminum hydroxide forms no salts. For instance, the carbonates and sulfides of many metals are precipitated from solution, but these salts of aluminum are not so precipitated. If aluminum sulfide, Al_2S_3, be formed by direct union of the heated elements and then added to water, it is completely hydrolyzed, with precipitation of the hydroxide:

$$Al_2S_3 + 3\ H_2O \rightarrow 2\ Al(OH)_3 + 3\ H_2S.$$

In fact, any attempt to precipitate aluminum sulfide by adding ammonium sulfide to a solution of an aluminum salt results only in precipitation of the hydroxide. If the sulfide forms at all, it is instantly hydrolyzed.

When it acts as an acid aluminum hydroxide is called aluminic acid, H_3AlO_3, and its salts aluminates such as Na_3AlO_3. By loss of water metaluminic acid, $HAlO_2$, may form. The most stable aluminates at high temperatures are the salts of the meta-acid:



The Spinels. — A mineral known as spinel is the magnesium salt of metaluminic acid, $Mg(AlO_2)_2$. Similar salts are known with other bivalent metals in place of the magnesium. All such are called spinels. Some are found in nature. Illustrations of such spinels are the following:

$Ca(AlO)_2$, found in Portland cement,
$Zn(AlO)_2$, the zinc ore, gahnite.

Also, the trivalent aluminum may be replaced by other trivalent elements, so that there are such substituted spinels as the following:

$Fe(CrO_2)_2$, chromite,
$Zn(FeO_2)_2$, franklinite,
$Fe(FeO_2)_2$, magnetite.

It is rather surprising to learn that magnetite, Fe_3O_4, is a ferrous salt of ferric acid.

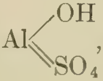
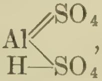
Aluminum Chloride, $AlCl_3$. — When aluminum or its hydroxide is dissolved in hydrochloric acid and the solution concentrated, crystals of the chloride, $AlCl.6H_2O$, are formed. Any attempt to secure the useful anhydrous salt by driving off the water fails. With rise in temperature hydrolysis increases, so that only the oxide and hydrochloric acid are formed:

$$2AlCl_3+3\ H_2O \rightarrow Al_2O_3+6\ HCl.$$

This reaction is really reversible and the water could be removed safely in a stream of dry hydrogen chloride. By mass action this would push the equilibrium to the left and yet remove the water. In actual practice it is simpler to leave water out of the situation. Dry chlorine, or even hydrogen chloride not quite dry, is passed through a tube containing hot aluminum. Aluminum chloride sublimes:

$$2\ Al+3\ Cl_2 \rightarrow 2\ AlCl_3,$$
$$2\ Al+6\ HCl \rightarrow 2\ AlCl_3+3\ H_2.$$

The anhydrous salt is very useful in some organic reactions. It fumes strongly in moist air, due to hydrolysis.

Aluminum Sulfate, $Al_2(SO_4)_3$. — The neutral sulfate, $Al_2(SO_4)_3$-18 H_2O, is formed by the neutralization of the base, aluminum hydroxide, by the equivalent quantity of sulfuric acid. Bauxite may be used. A basic salt,  $Al\genfrac{}{}{0pt}{}{\diagup OH}{\diagdown\!\!\diagdown SO_4}$, is produced if the base is in excess; and an acid salt,  $Al\genfrac{}{}{0pt}{}{/\!\!/ SO_4}{\diagdown SO_4}$ with $H{-}SO_4$, if the acid is in excess. This acid salt is interesting because its neutralization may be completed by potassium hydroxide, for example, in which case there is formed the double sulfate of potassium and alum, $KAl(SO_4)_2$, which crystallizes in splendid large crystals with twelve molecules of water of crystallization. This substance is the one originally known as alum.

The Alums. — Common alum, $KAl(SO_4)_2.12\,H_2O$, may be formed as above or by merely mixing solutions of potassium sulfate and aluminum sulfate in molecular proportions. On concentration the solution yields octahedral crystals. There are some deposits of a basic alum known as alunite in Utah, Italy, Hungary and many other places. Because many substituted alums are possible by replacing potassium with almost any univalent metal (Na, Cs, Rb, Ag, NH_4), this is sometimes distinguished as "potash alum." Still further substitution is possible, in that any trivalent metal may be used in place of aluminum. These all crystallize with twelve molecules of water and all have the same characteristic crystalline form. Consequently crystals containing a number of alums are possible or layers of one may form around another. Below are given some of the best known alums:

$NaAl(SO_4)_2.12\,H_2O$, Soda alum
$NH_4Al(SO_4)_2.12\,H_2O$, Ammonium alum
$KFe(SO_4)_2.12\,H_2O$, Iron alum
$NH_4.Cr(SO_4)_2.12\,H_2O$, Ammonium chrome alum

Exercise 1. — Why isn't the double sulfate formed by mixing solutions of ferrous sulfate, $FeSO_4$, and ammonium sulfate, $(NH_4)_2SO_4$, an alum?

Common alum has many uses but, for most of these the cheaper aluminum sulfate is just as good. The alums have one advantage for certain special uses — they crystallize better than the simple sulfate and consequently are more readily purified by fractional crystallization. Either alum or the plain sulfate is added to city water supplies to aid in removing suspended matter and bacteria. If the water be soft a little lime is added at the same time to insure precipitation of the gelatinous aluminum hydroxide. The bicarbonates of hard water serve as well as the lime:

$$Al_2(SO_4)_3+3\,Ca(HCO_3)_2 \rightarrow 3\,CaSO_4+2\,Al(HCO_3)_3,$$
$$Al(HCO)_3+3\,H_2O \rightarrow Al(OH)_3+3\,H_2CO_3.$$

In sizing paper to prevent the spread of ink it is the practice to mix an alkaline rosin soap in the pulp with aluminum sulfate. The resulting reaction yields free rosin throughout the paper where it is wanted. On passing through hot rolls the rosin melts throughout the paper.

Alum baking powders are essentially mixtures of alum and sodium bicarbonate. A solution of the alum in the wet dough is acid by hydrolysis and so reacts with the bicarbonate to release the carbon dioxide so essential in making dough porous. It may also be considered that aluminum bicarbonate is formed and hydrolyzed with evolution of carbon dioxide.

A number of aluminum salts are used as mordants, substances which fix the dye to the fiber.

Dyeing. — Of the three leading classes of fabrics, cotton, silk and wool, the silk and wool are the easiest to dye. This is because their fibers are protein material and more reactive chemically than the cellulose of cotton. Although a few thousand dyes are known, they may be grouped as follows:

1. *The indigo type.* Solutions of dyes readily penetrate any fiber but wash out again unless the dye be held as an insoluble compound. For example, a fabric may be soaked in a solution of lead acetate and then in a solution of sodium chromate. Lead chromate is precipitated throughout the fabric and cannot be washed out. Indigo is insoluble in water. To get it into the fabric in the first place it is necessary to reduce it by sodium hydrosulfite to the soluble, but colorless, indigo white. On exposing the fabric to the air this compound is oxidized to the insoluble blue indigo, now thoroughly entangled in every crevice and cell of the fibers.

2. *Direct dyes.* Solutions of direct dyes diffuse into fabrics and either react with the fiber or are adsorbed powerfully on all surfaces. They are sometimes salted out by addition of sodium sulfate. Direct dyes for wool and silk are numerous, but for cotton they are relatively few.

3. *Mordant dyes.* There are many beautiful dyes not retained by cotton without help. This help is secured by the use of aluminum hydroxide. Now this hydroxide is insoluble and hence cannot be worked into the fibers. However, if a solution of aluminum acetate penetrates the material, its natural hydrolysis can be increased by boiling or a base may be added. By this device the insoluble aluminum hydroxide is formed throughout the fiber. A soluble dye penetrating below the surface is held by the

hydroxide, so the dyed material becomes fast to washing. Other mordants are used, such as chromium hydroxide or even tannic acid. The latter material forms insoluble tannates with basic dyes. Mordant action can be demonstrated in a test tube. To a solution of alum and a dye add a base. Filter and wash the precipitate. It retains the dye. Such compounds are called *lakes* and in dyeing they are formed in the fiber.

Indigo is the greatest dye used. It was formerly made from a plant grown in India, but about 1897 a method was developed for preparing it from naphthalene. The natural product was almost driven from the market. Alizarin, a famous red dye, was formerly made from madder root but it, too, has become a synthetic product. There are still some important natural dyes, such as logwood and fustic, in use, but most dyes are derived from coal tar. The American dye industry has grown tremendously because of the war's stimulating effect and now there are very few of the former imported dyes not yet equaled or excelled in this country. The manufacture of military explosives and of dyes go hand in hand. They use the same raw materials to a marked extent and facilities for producing dyes are quickly adapted to the manufacture of explosives. Evidently our military preparedness in the future rests upon the existence of a prosperous dye industry.

Brick and Pottery. — Kaolin or china clay is the weathered residue from feldspar. Its composition is represented by $H_2Al_2(SiO_4)_2.H_2O$, while that of feldspar is $KAlSi_3O_8$. Common clay owes its color to impurities, usually oxides of iron. In burning brick or tile the impurities fuse and act as a bond for the clay particles. Fire brick, with its great infusibility, must be made from rather pure clay.

Porcelain is a fired mixture of kaolin and feldspar. The more fusible feldspar binds the kaolin particles and makes the mass translucent. When such ware is dipped into a water suspension of ground feldspar, dried and burned again, it receives a glaze of feldspar. Cheaper ware may be so porous that a glaze is absolutely essential, as in ordinary table dishes. If the glaze has a different coefficient of expansion from the body of the ware, it cracks with temperature changes.

Many principles of colloid chemistry apply to ceramics. Addition of a small amount of base to wet clay makes it more plastic.

Adsorption of $\overset{-}{OH}$ ions by the clay particles aids in dispersion. Consequently the wet clay can be made fluid enough for pouring into moulds with less water than if $\overset{-}{OH}$ ions were not present. Not only is the great shrinkage on drying and firing lessened, but the cost of water removal is lessened. In the Schwerin process of purifying clay a suspension in water is electrolyzed. Iron oxide particles are positively charged in water and migrate to the negative electrode, while the negatively charged clay particles migrate to the positive electrode.

Ultramarine. — A rare stone of beautiful blue color, lapis lazuli, was once so greatly prized that it sold for $60 per ounce. In 1828 Gmelin prepared it by heating a mixture of clay, sodium sulfate, carbon and sulfur. The mineral was represented as $(NaAlSiO_4)_4Na_2S_2$. It now sells for a few cents per pound under the name *ultramarine*. It is much used as a pigment in wall paper, water colors and laundry blueing, because it is very stable to the action of light and alkalies. Weak acids destroy the color and release hydrogen sulfide. It seems probable that the color is due to sulfur colloidally dispersed in the solid.

Portland Cement. — The Romans ground together volcanic ashes and lime with formation of a cement that, when mixed with water, set to a solid. Some specimens of this Puzzolan cement are still in good condition. To-day we do practically the same thing in grinding together blast furnace slag (granulated) and lime. But the best of these hydraulic cements is the modern Portland cement. The essential raw materials are clay and limestone. There must be present the equivalents in combined form of CaO, SiO_2 and Al_2O_3. In the Rosendale district of New York and elsewhere there are cement rocks which approximate this composition, but usually clay and limestone are used. The raw materials are finely ground, fired in a rotary kiln to incipient fusion (the edges of lumps just melting) and the clinkered product ground again. These rotary kilns are nearly horizontal, from 60 to 150 feet long and 6 to 9 feet in diameter (Fig. 108). They are heated with powdered coal (see copper smelting).

The materials enter at the cooler end, slowly working down to the end where the flame enters. The product is a calcium aluminate and calcium silicate. About 3 per cent of gypsum ($CaSO_4$) is added to retard setting. A little iron oxide and magnesium oxide are allowed, but there is a definite range of concentrations for all the constituents. The cement powder when used for walls, walks, etc., is mixed wet with sand and gravel as a filler. The cement is hydrolyzed with formation of crystals of calcium hydroxide and a colloidal mass of monocalcium silicate which cements together crystals of the aluminate and the hydroxide of calcium. The aluminum hydroxide produced is merely an impervious filler. In 1914 the United States produced 88,230,000 barrels of cement. The development of such a cheap and strong building material, easily and rapidly placed, has had a tremendous influence not merely on ordinary building but on vast engineering projects as well.

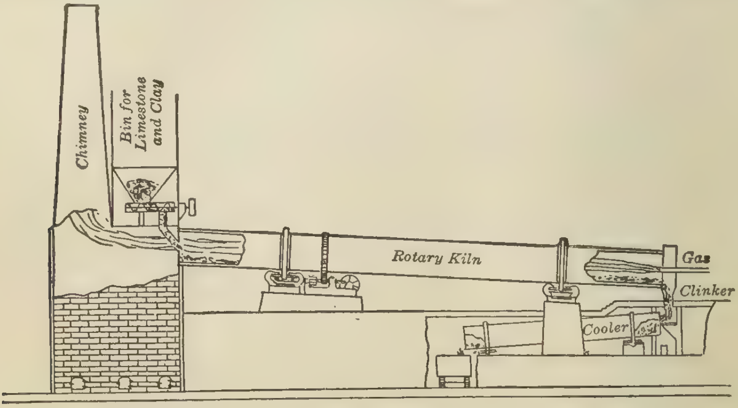


Fig. 108

The Rare Earths

At the left of the fourth column of the periodic table there are four elements, scandium, yttrium, lanthanum and ytterbium, which are members of a group of sixteen elements called the "Rare Earths." The oxides of these elements as regards basicity lie approximately between the oxides of the alkaline earths and the trivalent metals, aluminum, iron and chromium. With the exception of cerium in the ceric salts and of the recently prepared samarium and europium dichlorides, these elements are mostly trivalent and their salts are only slightly hydrolyzed in water. The elements are so much alike that their separation is most difficult.

Interest in the rare earths was very dull before Auer von Welsbach (1884) invented the incandescent gas mantle that bears his name. He found that a mixture of the oxides of thorium and cerium in the proportion of 99 to 1 by weight became incandescent at comparatively low temperatures. It was only a step in advance to prepare fabric mantles of combustible material, impregnate them with a solution of the nitrates and on burning secure an ash of the oxides. This mantle in a gas flame gives off far more light than the same flow of gas can yield burning in an open jet. Welsbach's invention has been a genuine contribution to the comfort and economy of life. Several minerals contain cerium, but the chief commercial source is monazite sand, mined in Brazil, India, and to a slight extent in the United States. In these sands the percentage of thoria (the oxide) runs from 2.3 to 28. The ceria averages 30 per cent. Other rare earth oxides, especially lanthana, neodymia, yttria, and praseodymia are present. Since but little ceria is needed in gas mantles, it is evident that the most valuable constituent of the monazite is thoria and that the greater part of the ceria is thrown away. In 1918 the United States used 88,000 tons of this sand in the preparation of many millions of mantles. The most successful utilization of the monazite residues has been in the preparation of "misch metal" by the electrolysis of the fused chlorides. This misch metal when alloyed with iron or other hard metals emits a shower of sparks when scratched. For this property it is much used in friction gas lighters and cigar lighters. Bullets or shells containing some cerium or misch metal leave a luminous path of sparks.

During the Great War this country produced nearly 2000 pounds of cerium per month. With peace the demand collapsed. Now the problem is to extend the uses of this and the other rare earths. In the flaming arc the carbon core may contain such salts as cerium fluoride. Small pencils of thoria are used in searchlights. The latest form of the Nernst lamp contains rare earth oxides. Cerium or thorium salts in flashlight powders increase the brilliancy of the burning magnesium. Glasses and enamels receive interesting properties from the rare earths. Neodymium salts, in particular, produce a number of beautiful colors in enamels. Other uses are found in photography and in the textile trade. In medicine some rare earth salts have found favor. A mixture of cerium earth oxalates is given to prevent nausea in sea sickness and epilepsy. Cerium salts are effective catalysts in the manufacture of sulfuric acid, in Deacon's process and for other reactions. Misch metal is a more powerful reducer than aluminum in the Goldschmidt process, but, unfortunately, more costly. With such a powerful reducing action cerium may come into use as a deoxidizer of steel.

These uses are detailed in order to stress the fact that all elements are either useful or potentially useful. A list of the rare earth metals with atomic weights follows:

Scandium	45.1	Gadolinium	157.3
Yttrium	89.3	Terbium	159.2
Lanthanum	139.0	Dysprosium	162.6
Cerium	140.3	Holmium	163.5
Praseodymium	140.9	Erbium	167.6
Neodymium	144.3	Thulium	168.5
Samarium	150.4	Ytterbium	173.5
Europium	152.0	Lutecium	175.0

Gallium, Indium, and Thallium

These three elements occur on the right side of the fourth column of the periodic table, but as yet they are of little consequence. Gallium and indium occur in zinc blende; gallium is also found in bauxite. Gallium (at. wt. 70.1), as a metal, closely resembles aluminum. Its hydroxide, $Ga(OH)_3$, is amphoteric and the sulfate forms alums. (The rare earths do not form alums.)

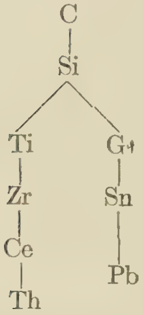
Indium (at. wt. 114.8). — This element is a very malleable metal, easily soluble in hydrochloric acid, and, unlike aluminum, readily attacked by nitric acid. Although usually trivalent, a mono- and a dichloride exist. Indium resembles iron in many of its compounds. Its hydroxide is amphoteric and its sulfate forms alums.

Thallium (at. wt. 204). — Thallium is obtained from the flue dust of sulfuric acid plants, since it occurs in some sulfides. As a univalent element it forms the soluble strong base, $TlOH$, and a soluble carbonate, sulfate, and phosphate. In this series it resembles the alkalies or silver and as a univalent element forms alums. The chloride is rather insoluble and is affected by light. As a trivalent element it does not form alums, nor is the hydroxide, $TlO.OH$, soluble in bases.

CHAPTER XXXIV

TIN AND LEAD

The Group



This group, standing at the middle of the periodic chart, contains elements with decidedly weak basic and acidic properties. The hydroxides of carbon and silicon are weak acids. The subgroup on the left of the column contains the rare elements titanium, zirconium, cerium and thorium. The first two are feebly acid-forming as well as feebly base-forming; the last two are only base-forming. On the right, germanium, tin and lead show basic properties in the lower oxides and acidic properties in the higher oxides. The group as a whole is quadrivalent, but all the elements exhibit another valence (two) with the exception of cerium, which may be trivalent. Tin and lead, because of their familiar occurrence, are the only elements which invite a close study.

Tin

Occurrence. — Tin ores are so easily smelted that the metal was known to the ancients. It was brought by the Phœnicians to Egypt and to Greece from the "Islands of the Cassiterides" now known as the British Isles. The tin mines of Cornwall have been, up to recent times, the chief source of this metal. At present most of it comes from the East Indies, although Bolivia, Tasmania, and Britain still produce. About 100 tons yearly come from Alaska, but this is negligible. Deposits have been found in Nigeria, but are not worked yet. The chief ore, almost the only ore, is the crude dioxide, SnO_2, called cassiterite or tin stone.

Metallurgy. — All tin ores are concentrated by washing away the gangue and are then roasted in long rotary kilns like Portland cement kilns. By this process sulfur is oxidized to the dioxide. Arsenic is oxidized to the trioxide, which is collected in a cooling chamber — later to be sold as a valuable by-product. After this preliminary roasting the tin oxide is heated with carbon in a furnace, where it is reduced to the metal. In order to separate the tin from the bismuth, zinc, copper, and iron, which are usually present in it, advantage is taken of the surprisingly low melting point of the pure metal, 232°. The foreign metals are present as higher melting tin alloys. The mass is heated hot enough to melt pure tin, but not hot enough to melt the alloys. The pure liquid tin is poured off. This process of "liquation" is repeated many times while the dross is thrown back to be reduced. By another process the reduced ore is melted in a small reverberatory furnace. This produces a slag containing most of the impurities, and a metal, which is cast into anodes for electrolytic refining.

In 1910 the world produced 115,589 tons of tin, the United States using nearly half this amount.

Properties. — Tin is a white metal melting at 232° and boiling at 2275°. Its density averages 7.3. Below 18° tin tends to change into a gray powder with increase in volume. This change is most rapid at about $-48°$ and when the metal is in contact with some of the gray modification. This "tin disease" was first observed when some organ pipes in the northern part of Russia during prolonged cold weather crumbled to dust. At another time, block tin stored in Petrograd developed this disease. It must be admitted that this change is rare, but if held at very low temperatures and inoculated with the gray powder all ordinary tetragonal tin would change. Tin is most malleable at 100°, while at 200° it is so brittle that it can be ground to a powder. (What other metals become brittle when heated?) Tin is plated on thin sheets of iron or steel by mere dipping of the clean steel into melted tin. The sheet must first be carefully pickled to free it from all oxides of iron. The modern ideal in tin-plating is to secure as thin a coating of tin as possible, without holes or cracks. From such tinned sheets are made common tin cups, pails, pans and a hundred cheap and useful articles. Our dependence upon tin will become evident to all if this country is ever blockaded for a considerable period, as was Germany. Then the canned food industry will have to rely upon glass; soldering of metal joints will be impossible; and substitutes for a great number of common tin utensils will have to be prepared. Tin is essential in soft solder and in bronze. When a tin rod is bent rapidly the crystals of tin grate on one another and give forth a sound called the "tin cry."

Chemically, tin is not very active. It is affected neither by the moisture nor by the carbonic acid of air and is therefore slowly tarnished. It is this property that makes it so useful. In acids the metal dissolves slowly. Dilute nitric converts it into stannous nitrate, $Sn(NO_3)_2$, with evolution of hydrogen. Rather concentrated nitric acid converts tin into an insoluble oxide, SnO_2. Dry chlorine attacks the metal much more readily than it does iron, so tin scrap is treated with chlorine. Anhydrous stannic chloride, $SnCl_2$, is secured.

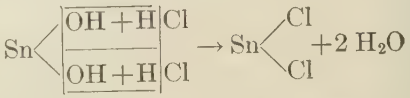
Iron is between zinc and tin in activity, so it is interesting to compare the wearing qualities of galvanized iron and tinned iron. Since zinc is more active than iron, it is the first to go when a crack or puncture exposes both metals to the attack of moisture and carbon dioxide. In such a galvanic couple the more active element dissolves first. Not so with tin. A puncture or crack means the rapid loss of iron, more rapid than if the tin coating had never been there. Of these two the iron is the more active. So tin plate is excellent until the iron is exposed, and then it is worse than no plate.

STANNOUS COMPOUNDS

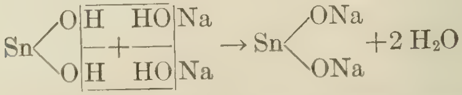
When tin is dissolved in acids the hydrogen evolved insures the formation of salts of the lower valence. The same is true of iron and other metals, which exhibit two valences. If any stannic chloride were formed it would be reduced by the nascent hydrogen:

$$Sn + 2\,HCl \rightarrow SnCl_2 + H_2,$$
$$Fe + 2\,HCl \rightarrow FeCl_2 + H_2,$$
$$SnCl_4 + 2\,H \rightarrow SnCl_2 + 2\,HCl.$$

Stannous Oxide and Hydroxide. — Stannous chloride reacts with a solution of sodium hydroxide to form the white, gelatinous hydroxide, $Sn(OH)_2$. The oxide, SnO, is a black powder precipitated by adding warm stannous chloride to a solution of sodium carbonate. When dry it can be burned in the air. Stannous hydroxide is much like zinc hydroxide and aluminum hydroxide in that it dissolves in strong acids as well as in strong bases. Therefore it is amphoteric.



$$\mathrm{Sn}\begin{matrix}\mathrm{OH+H\,Cl}\\ \mathrm{OH+H\,Cl}\end{matrix} \rightarrow \mathrm{Sn}\begin{matrix}\mathrm{Cl}\\ \mathrm{Cl}\end{matrix} + 2\,H_2O$$



$$\mathrm{Sn}\begin{matrix}\mathrm{O\,H + HO\,Na}\\ \mathrm{O\,H + HO\,Na}\end{matrix} \rightarrow \mathrm{Sn}\begin{matrix}\mathrm{ONa}\\ \mathrm{ONa}\end{matrix} + 2\,H_2O$$

The soluble salt, $Sn(ONa)_2$, is called sodium stannite, which suggests that stannous hydroxide may also be termed *stannous* acid.

Stannous Chloride, $SnCl_2$. — A solution of this salt is prepared by dissolving tin in hydrochloric acid. The anhydrous salt, however, is made by passing hydrogen chloride over hot tin. The solutions are acid by hydrolysis. "Tin salt," used as a mordant in dyeing, is $SnCl_2 . 2\,H_2O$. Its solution is a good reducing agent. For example it reduces mercuric chloride to metallic mercury:

$$(1)\quad SnCl_2 + 2\,HgCl_2 \rightarrow 2\,HgCl + SnCl_4,$$
$$(2)\quad SnCl_2 + 2\,HgCl \rightarrow 2\,Hg + SnCl_4.$$

Stannous Sulfide, SnS. — This insoluble brown-black sulfide is precipitated by hydrogen sulfide from solutions of stannous salts:

$$SnCl_2 + H_2S \rightarrow SnS + 2\,HCl.$$

As this reaction shows, it is not dissolved by dilute acids. However, it is soluble in concentrated hydrochloric acid. Unlike the lower sulfides of arsenic and antimony, it is not soluble in the simple alkali sulfides. With polysulfides it forms the soluble sulfostannates so important in qualitative analysis:

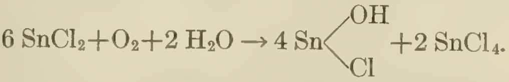
$$SnS + Na_2S_2 \rightarrow Na_2SnS_3.$$

On boiling some time with sodium sulfide, Na_2S, some stannic sulfide, SnS_2, is formed, and this reacts with the sodium sulfide to form the same product as above:

$$SnS_2+Na_2S \rightarrow Na_2SnS_3.$$

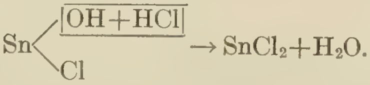
Stannic Compounds

A solution of stannous chloride is partially oxidized in air with formation of stannic chloride and the basic chloride of stannous tin:



$$6\ SnCl_2+O_2+2\ H_2O \rightarrow 4\ Sn\left\langle\begin{matrix}OH\\Cl\end{matrix}\right.+2\ SnCl_4.$$

By addition of acid this basic chloride is converted into stannous chloride:



$$Sn\left\langle\begin{matrix}\boxed{OH+HCl}\\Cl\end{matrix}\right. \rightarrow SnCl_2+H_2O.$$

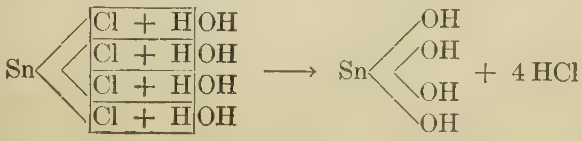
The only way to keep a solution of a stannous salt is to have a few pieces of metallic tin and some acid present. The metal acts as a reducing agent, as does the hydrogen released.

Stannic compounds are not easily obtained from the dioxide, SnO_2, because this oxide is attacked with difficulty by acids. They are obtained indirectly from metallic tin or from stannous compounds.

Stannic Chloride, $SnCl_4$. — Stannic chloride is prepared in solution by passing chlorine into a solution of stannous chloride:

$$SnCl_2+Cl_2 \rightarrow SnCl_4.$$

The anhydrous form is made by passing chlorine over hot tin. (See recovery from tin scrap.) It is a colorless liquid, fuming in moist air and boiling at 114°. It is a good solvent for sulfur, iodine and phosphorus. With a little water it forms solid hydrates such as $SnCl_4.5\ H_2O$, "oxymuriate of tin," which is used as a mordant in dyeing. On addition of more water, these hydrates dissolve. The solution slowly becomes turbid on boiling with precipitation of part of the stannic hydroxide formed. The rest remains in colloidal suspension.



$$Sn\left\langle\begin{matrix}\boxed{Cl+H}OH\\\boxed{Cl+H}OH\\\boxed{Cl+H}OH\\\boxed{Cl+H}OH\end{matrix}\right. \longrightarrow Sn\left\langle\begin{matrix}OH\\OH\\OH\\OH\end{matrix}\right.+4\ HCl$$

Tin tetrachloride unites with hydrochloric acid to form chlorostannic acid, H_2SnCl_6 (equivalent to $2\,HCl.SnCl_4$), which forms crystalline soluble salts with the alkalies, $(NH_4)_2SnCl_6$, or "pink salt," for example. A freshly prepared solution of stannic chloride is a poor conductor of electricity (only slightly ionized), but later its conductivity improves with its increase in acidity. Gradual hydrolysis with formation of the good conductor, hydrochloric acid, explains this peculiar action. All stannic solutions are considerably hydrolyzed, the nitrate and the sulfate even more than the chloride.

EXERCISE 1. — If you added bromine water to a solution of stannous chloride, how would you know when all the tin was oxidized? Write the equation.

α-Stannic Acid, H_2SnO_3. — The alpha form of stannic acid is readily prepared by addition of ammonium hydroxide or sodium hydroxide to a solution of a stannic salt. We might expect $Sn(OH)_4$, but this loses water and yields H_2SnO_3. The rest of the water may be driven off and the anhydride, SnO_2, secured. The white gelatinous precipitate of α-stannic acid dissolves readily in excess alkali, forming stannates such as Na_2SnO_3. The acid also dissolves easily in dilute mineral acids.

Sir William Perkin invented a method of fireproofing cotton flannel clothing by the use of stannic acid. He wished to enable the poor to wear cheap, warm underclothing without fire risk. The fabric soaked in a solution of sodium α-stannate is washed, dried and dipped in ammonium sulfate solution. The ammonium stannate formed is hydrolyzed, so stannic acid is precipitated in the fibers and cannot be washed out.

β-Stannic Acid, $(H_2SnO_3)_5$ (Metastannic acid). — When slightly diluted nitric acid reacts with tin, a hydrated form of the dioxide is produced as a white, insoluble powder. This form of stannic acid, unlike the alpha, is almost insoluble in dilute mineral acids. It is not readily attacked by alkalies, but if fused with sodium hydroxide it is converted into sodium α-stannate, identical with the salt secured by using the simple dioxide.

The dilute solution of the α-compounds gradually change into β-compounds, more quickly on boiling. The β-compounds are converted into α-compounds by boiling with concentrated hydrochloric acid, or with concentrated potassium hydroxide.

Stannic Sulfide, SnS_2. — On heating tin dust with sulfur and ammonium chloride a product called "mosaic gold" is formed. It is much used in gilding radiators, etc. This is really stannic sulfide. It can also be formed by passing hydrogen sulfide into a solution of a stannic salt. The precipitate dissolves in alkali sulfides, yielding sulfostannates:

$$SnS_2 + Na_2S \rightarrow Na_2SnS_3.$$

Tests. — Tin compounds are usually recognized by converting them into stannous chloride which reduces mercuric chloride to white, insoluble mercurous chloride and black finely divided mercury. The brown-black stannous sulfide, soluble in polysulfides, and the yellow stannic sulfide, soluble in alkali sulfides, are both well known in analysis. The ease of reduction of the oxide by hot carbon is noteworthy.

LEAD

Occurrence. — Like tin, lead was known to the ancient Egyptians because of the ease with which its ores were smelted. The Romans used lead pipes for water service. The sulfide, PbS, or galena, is the most important ore, although cerussite, $PbCO_3$, anglesite, $PbSO_4$, and crocoite, $PbCrO_4$, are found. Lead ores are common all over the world. In 1917 the world production of the metal reached 580,000 tons, of which the United States produced 34 per cent. Australia ranks second, with Spain third. One chief lead district is in Missouri. Other fields are in Idaho, Utah and Colorado.

Metallurgy. — The older reverberatory smelter has been displaced by the blast furnace. Part of the lead sulfide is first roasted to convert it into the oxide. This is then mixed with the raw ore, coke and limestone, and added to the blast furnace, where it meets a strong blast of air. The burning carbon and the carbon monoxide formed are both good reducing agents, as we shall learn in connection with the smelting of iron ores. Lead oxide is reduced to the metal:

$$(1)\quad 2\,PbS + 3\,O_2 \rightarrow 2\,PbO + 2\,SO_2,$$

$$(2)\quad 2\,PbO + C \rightarrow 2\,Pb + CO_2,$$

$$(3)\quad PbO + CO \rightarrow Pb + CO_2.$$

The iron present as an impurity is burned to the oxide and, as we shall also learn in the study of the iron blast furnace, it is reduced by hot carbon monoxide to the metal. But iron can extract sulfur from lead sulfide, so in this case an impurity is a genuine aid:

$$(4)\quad Fe_2O_3+3\,CO \rightarrow 2\,Fe+3\,CO_2,$$
$$(5)\quad PbS+Fe \rightarrow Pb+FeS.$$

Another view of these reactions is that the lead sulfide burns to lead sulfate, which is able to react with more raw sulfide ore to their mutual advantage. Still another theory is that some lead oxide formed in roasting oxidizes the sulfide:

$$PbS+PbSO_4 \rightarrow 2\,Pb+2\,SO_2,$$
$$PbS+2\,PbO \rightarrow 3\,Pb+SO_2.$$

The limestone carries off silica in the fusible slag, calcium silicate. A molten "matte" of iron sulfide with copper sulfide and some lead sulfide is separated for further extraction of lead.

Refining of lead usually involves the separation of antimony, arsenic, bismuth, and copper by oxidation. The lead is kept molten with stirring. These impurities oxidize more readily than lead and float to the surface as dross. Any gold or silver may be removed by Parkes' process (see silver) or by Betts' electrolytic process. With a lead silicofluoride ($PbSiF_6$) bath containing a little glue to insure coherence of deposit, the crude lead slabs are hung as anodes and thin sheets of pure lead as cathodes. With electrolysis the impurities drop as anode mud (compare with purification of copper). If antimony, arsenic and copper were not removed, the lead would be hard and this would greatly cripple the usefulness of the element. We want some metals to be extremely hard and others to be extremely soft.

Properties. — Lead is a heavy metal of specific gravity 11.4, soft and easily cut with a knife. The metal melts at 327° and boils at 1525°. Just below its melting point it can be squeezed into tubes. When freshly cut, its luster is bright, but the surface quickly tarnishes with formation of oxide and basic carbonate. This coating protects the metal from further oxidation, although it detracts sadly from the real beauty of lead. A strip of zinc hung in a very dilute solution of a lead salt (acetate or nitrate) is soon covered with a "lead tree" of beautiful gleaming crystals of metallic lead:

$$\overset{++}{Pb}+Zn+\overset{-}{NO_3}+\overset{-}{NO_3} \rightarrow \overset{++}{Zn}+Pb+\overset{-}{NO_3}+\overset{-}{NO_3}.$$

Chemically lead does not always seem as active as it really is. For example, cold hydrochloric acid scarcely attacks it. Lead chloride forms a protective coating over the lead. Hot acid dissolves this and permits the metal to be attacked. Lead sulfate, too, is insoluble and has a protecting action. But when above 80 per cent in concentration, sulfuric acid dissolves lead sulfate and consumes the metal. Nitric acid dissolves lead with release of oxides of nitrogen rather than hydrogen. Acetic acid slowly attacks lead in the air, due to the preliminary oxidation of the metal. This reaction is fundamental in the paint industry.

Solutions of lead salts are extremely poisonous, so that water conducted through lead pipes may produce lead poisoning. This is particularly true of soft water, which with air forms $Pb(OH)_2$, somewhat soluble. Hard water is much less dangerous because it soon forms a coating of insoluble carbonate and sulfate on the lead. Therefore, a bright lead pipe is under suspicion. The worst feature of lead poisoning is that it is cumulative. Traces of lead may be taken into the body for years, but they remain. Painters and workers in lead industries have to be careful not to convey lead compounds to the mouth through any lack of care in washing the hands.

Exercise 2. — Why are we able to make sulfuric acid in lead chambers without loss of lead?

Lead is the cheapest metal after iron. Its resistance to the attack of moist air and of several acids makes it useful in lining vats or tanks. Sulfuric acid plants are lined with it, water pipes are made of it and shot and bullets are largely lead. Solder is an alloy of lead and tin; Babbitt (antifriction bearing metal) is a lead alloy; type metal contains it; and the collapsible metal tube containers for pastes are lead alloys. Storage batteries use lead plates and all lead paints begin with lead as raw material.

Oxides. — There are five oxides of lead, although only two are in common use:

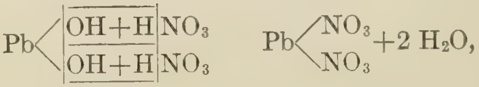
Pb_2O, lead suboxide, gray,
PbO, lead monoxide (litharge), yellow-red,
Pb_2O_3, lead trioxide, orange yellow,
PbO_2, lead dioxide or peroxide, chocolate brown,
Pb_3O_4, lead tetroxide (minium or red lead), red.

The suboxide is scarcely worth discussion. It is possible that it is merely $PbO+Pb$. It is probably the oxide found on the surface of freshly tarnished lead. By heating gently dry lead oxalate it may be formed in quantity:

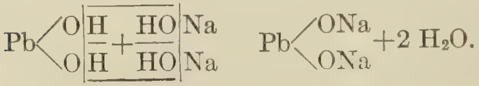
$$2\ PbC_2O_4 \rightarrow Pb_2O+3\ CO_2+CO.$$

Lead Monoxide (Litharge), PbO. — This yellow-red powder is obtained by heating lead in the air. It would probably be yellow, but for more or less red lead, Pb_3O_4, also formed by heating lead in air. Above 600° all lead oxides pass into the monoxide. It is used in glazing pottery, making glass (of the cut-glass type) and is a starting point in preparing other lead compounds.

Lead oxide is the anhydride of $Pb(OH)_2$, sometimes called plumbous hydroxide, and sometimes plumbous acid. It is precipitated by the union of $\overset{++}{Pb}$ ions and $\overset{-}{OH}$ ions. With acids and alkalies it reacts like zinc hydroxide, yielding soluble lead salts or soluble plumbites:



$$Pb\left\langle\begin{array}{l|l}\overline{OH+H} & NO_3\\ \underline{OH+H} & NO_3\end{array}\right. \qquad Pb\left\langle\begin{array}{l}NO_3\\NO_3\end{array}\right.+2\ H_2O,$$



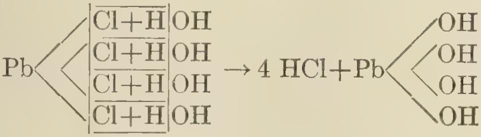
$$Pb\left\langle\begin{array}{l|l|l}O & \overline{H\ \ \ \ HO} & Na\\ O & \underline{H\ \ \ \ HO} & Na\end{array}\right. + \qquad Pb\left\langle\begin{array}{l}ONa\\ONa\end{array}\right.+2\ H_2O.$$

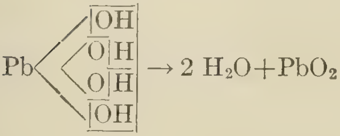
Exercise 3. — How does the existence of lead carbonate in water suspension show that $Pb(OH)_2$ is not an extremely weak base?

Lead Dioxide, PbO_2. — The simplest method of preparation is to add bleaching powder to a solution of sodium plumbite:

$$Ca(ClO)Cl+Na_2PbO_2+H_2O \rightarrow PbO_2+CaCl_2+2\ NaOH.$$

The chocolate-brown powder is a powerful oxidizing agent. Hydrogen sulfide gas passed over it is ignited. It may be considered the anhydride of plumbic acid (or hydroxide), $Pb(OH)_4$. This is apparent if the double salt, $2\ NH_4Cl.PbCl_4$, be added to water. The hydroxide formed by hydrolysis of the chloride immediately loses water and only the dioxide is precipitated. To be exact, the complete loss of water does not occur below 100°. An intermediate product is H_2PbO_3:





Lead tetrachloride is an unstable yellow oil. It is formed when a suspension of lead dichloride in concentrated hydrochloric acid is oxidized by a stream of chlorine. Addition of ammonium chloride to the cold solution yields the insoluble, stable yellow powder, $2\ NH_4Cl.PbCl_4$.

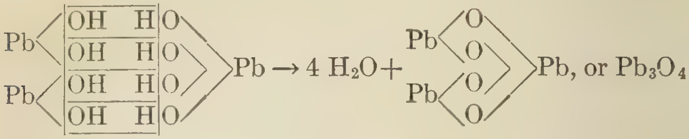
Lead disulfate, $Pb(SO_4)_2$, is similar to the tetrachloride in its excessive hydrolysis. It is formed by the electrolysis of cold, concentrated sulfuric acid at the lead anode. With water it is completely hydrolyzed to the dioxide.

Red Lead, Pb_3O_4. — Red lead, or minium, is prepared by carefully heating litharge, PbO, in air not higher than 545°. Above that temperature it decomposes into the monoxide and oxygen.

$$\underset{\text{(above 545°)}}{6\ PbO+O_2} \leftrightarrows \underset{\text{(below 545°)}}{2\ Pb_3O_4}.$$

It is used in considerable quantities as a pigment in red paints and also as an oxidizing agent.

A hint as to the real structure of red lead is obtained by treating it with nitric acid. Only two thirds of the lead is converted into lead nitrate; the other third being left as a residue of lead dioxide. Since nitric is an acid it is to be supposed that it dissolves the basic portion and leaves the acidic portion. We might imagine red lead to be $2\ PbO.PbO_2$. Now PbO is the anhydride of $Pb(OH)_2$, while PbO_2 is the anhydride of $Pb(OH)_4$. It is permissible, then, since the lower hydroxide is the more basic and the higher hydroxide the more acidic, to consider red lead a salt:



Call $Pb(OH)_2$ plumbous hydroxide, a base, and $Pb(OH)_4$ orthoplumbic acid. Then Pb_3O_4 could be named plumbous orthoplumbate.

The Halides of Lead. — Lead chloride, formed by the union of $\overset{++}{Pb}$ ions and $\overset{-}{Cl}$ ions or by the action of hot concentrated hydrochloric acid on the monoxide or carbonate, is somewhat soluble in hot water, but only sparingly soluble at room temperatures. On cooling the hot water solution white crystals separate. It is much more spectacular to cool a hot water solution of the yellow lead iodide, PbI_2. Beautiful gleaming gold crystals settle like so many spangles. The bromide is much like the chloride and iodide in solubility. All these halides of lead form complex salts with the alkali halides (compare with mercuric halides). In a previous paragraph the salt, $(NH_4)_2PbCl_6$, or $2\,NH_4Cl.PbCl_4$, was discussed.

Other Lead Salts. — ***Lead nitrate,*** $Pb(NO_3)_2$, is prepared from the metal or the monoxide by addition of nitric acid. It is colorless and very soluble. ***Lead acetate,*** $Pb(C_2H_3O_2)_2.3\,H_2O$ is made from acetic acid and lead. It was called "sugar of lead" because of its sweet taste. It is none the less poisonous because of this taste. If litharge be boiled with acetic acid a soluble basic acetate, $Pb\langle{}^{OH}_{C_2H_3O_2}$, is formed. ***Lead chromate,*** $PbCrO_4$, is the product of the union of $\overset{++}{Pb}$ ions with $\overset{--}{CrO_4}$ ions ($Pb(NO_3)_2+K_2CrO_4+ \rightarrow PbCrO_4+2\,KNO_3$). It is insoluble and yellow. As the pigment, "chrome yellow," it has value in the paint industry. Boiled with a solution of sodium hydroxide, it is converted into *chrome red*, $PbCrO_4.PbO$. ***Lead sulfide,*** PbS, occurs as the beautiful mineral galena. In laboratory precipitation it is black and amorphous, insoluble in cold dilute acids or bases. ***Lead sulfate,*** $PbSO_4$, is white and comparatively insoluble in water. It is more insoluble in alcohol. Sulfuric acid above 80 per cent concentration dissolves it, because of the formation of the soluble acid sulfate, $Pb(HSO_4)_2$.

White Lead. — A paint is prepared by grinding some heavy insoluble *pigment* of sufficient covering power with linseed oil. The drying of paint is not really a loss of water, but oxidation of the oil with formation of a tough, solid film. This oxidation of the oil is hastened by catalytic dryers made by boiling manganese dioxide, etc., with linseed oil. Among the pigments used are white lead, red lead, barium sulfate, lead chromate, zinc oxide, lithopone, iron oxides and others, but the one most used is white lead or basic lead carbonate, $Pb(OH)_2.2\ PbCO_3$. In the United States alone 150,000 tons are used annually. It is made by two or three methods, but only the famous old Dutch process need be considered here.

The Old Dutch Process. — Perforated sheets of lead called "buckles" (Fig. 109) are piled on the upper part of earthenware pots which are partly filled with dilute acetic acid. These pots rest on moist spent tan bark. They are covered with boards, on which is spread another layer of tan bark, and on this another series of pots. In this way a closed room is filled to the roof. The fermentation of the tan bark furnishes heat to volatilize the acetic acid and carbon dioxide to react with the basic lead acetate produced. The final product is basic lead carbonate. After several weeks the lead buckles, or what is left of them, are removed, run through rolls to flatten bits of lead so they may be caught by screens, and the white pigment sifted out. After grinding in oil the paint is ready for use.

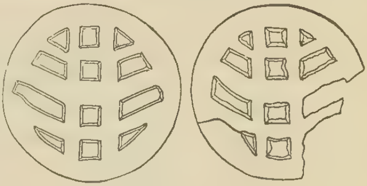


FIG. 109

The Lead Storage Battery. — A charged lead storage cell consists of a lead plate surfaced with lead peroxide as the positive pole and a second lead plate surfaced with spongy lead as the negative pole: both immersed in 20 per cent sulfuric acid.

When the two poles are connected by a metallic circuit the hydrogen ions give up their charge to the lead peroxide plate, reducing it to the monoxide, which at once reacts with sulfuric acid to form lead sulfate (Fig. 110).[1] The positive charge given to the

---

[1] In terms of the electronic conception of electricity it could be stated that the sulfate ions give two electrons each to the lead plate. Lead sulfate is then formed. The electrons travel through the wire to the other plate. These two electrons reduce the lead peroxide molecule to lead oxide, which readily reacts with sulfuric acid. For the present it is probably best to adhere to the older explanation.

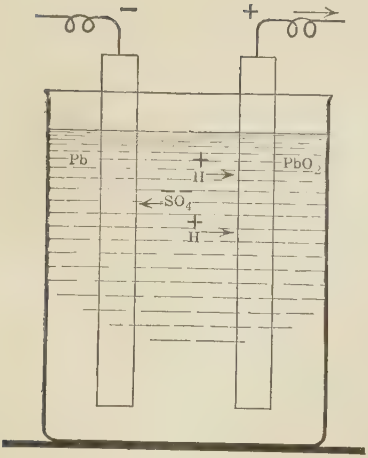


Fig. 110

plate spreads over the metallic circuit to the other pole, where it neutralizes the charge on sulfate ions in the adjoining layer of solution with formation of lead sulfate. Thus both plates become sulfated and the solution loses sulfuric acid:

$$PbO_2+2\ H \rightarrow PbO+H_2O,$$
$$PbO+H_2SO_4 \rightarrow PbSO_4+H_2O.$$

To charge a run-down cell (Fig. 111), current is led in at the anode. This pole being positive (as in electrolysis) attracts $\overset{--}{SO_4}$ ions, which on discharge oxidize the lead sulfate to lead disulfate. By hydrolysis this becomes the peroxide. The negative pole, which we may as well call the cathode during charging, attracts $\overset{+}{H}$ ions which, on discharge, reduce the lead sulfate to sponge lead. One plate becomes lead peroxide and the other sponge lead, while the solution gets back the sulfuric acid it lost on discharge:

$$PbSO_4+(SO_4) \rightarrow Pb(SO_4)_2,$$
$$Pb(SO_4)_2+2\ H_2O \rightarrow PbO_2 +2\ H_2SO_4,$$
$$PbSO_4+2\ H \rightarrow Pb+H_2SO_4.$$

The action in charging is just the opposite of that in discharging. It is chemical energy that is stored up, not electrical. If lead sulfate were formed by other means than the discharge of a storage cell, much heat would be released. With this battery all that energy is converted into electricity. In practice it is unwise to convert too thick a layer of the plates into lead sulfate, for

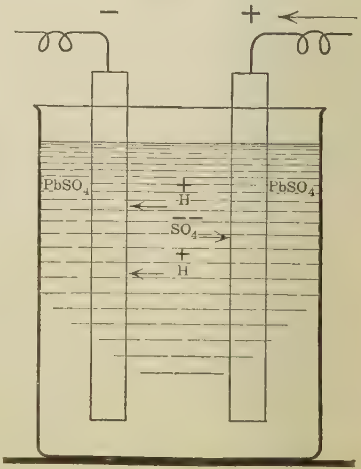


Fig. 111

regeneration becomes difficult, possibly due to a lack of permeability. Nor should a discharged cell stand long before charging. Otherwise the lead sulfate coating becomes more compact. The normal voltage of such a cell, fully charged, is about two volts, but this falls on discharge. Thus there are two ways of learning the condition of the cell: measuring the density of the acid and the potential fall between the poles.

Storage cells are used in submarines, in small isolated lighting plants, for ignition in gasoline engines, for self-starters in autos, and for many other purposes where direct current is needed.

Titanium

This element is quite common, being widely distributed in small quantities. It forms about 0.5 per cent of all soil and is found in minerals in connection with iron ores. In fact, vast iron ore beds in the United States are rendered unsuitable for present methods of smelting because of the presence of titanium. As our better ores are exhausted suitable means of utilizing the iron-titanium ores will, no doubt, be devised. The chief ores of this element are rutile, TiO_2, and ilmenite, $FeTiO_3$. Because of its high fusion point and strong affinity for nitrogen, carbon and oxygen, pure titanium has been difficult to prepare. Hunter made the first pure titanium (1900) by reduction of the tetrachloride with sodium. The element resembles polished steel in color. It is hard and brittle when cold, but is malleable at a low red heat. No wire has yet been made. Acids dissolve the metal. When hot it unites with oxygen, the halogens, sulfur, carbon and nitrogen.

Among its compounds are the dioxide, TiO_2, the nitride, TiN, the chloride, $TiCl_4$, and fluotitanic acid, H_2TiF_6. Rutile is used in coloring china and artificial teeth. Ferro-alloys of titanium (prepared by reduction in the electric furnace or by the aluminothermic process) are added to steel to remove oxygen at the moment of casting.

Zirconium

This element occurs in the mineral zircon, $ZrSiO_4$, and as the dioxide. The element has a high melting point. When hot it combines readily with oxygen, nitrogen and carbon. Consequently it is difficult to prepare. Hydrofluoric acid and aqua regia are the only acids that attack it. The dioxide with a melting point of 3000° has some use as a refractory material for furnace linings. Since its coefficient of expansion is very small bricks made of the dioxide stand sudden changes in temperature.

Thorium

Cerium was discussed in connection with the rare earths. Monazite sand, it will be recalled, is a mixture of the phosphates of thorium, cerium and other rare elements. From this sand thorium is extracted and converted into the soluble nitrate, $Th(NO_3)_4.6\ H_2O$, to be mixed with cerium nitrate for the preparation of Welsbach gas mantles. On burning the mantle only the incandescent ash of thorium oxide (99 parts) and cerium oxide (1 part) is left. The world uses 300,000,000 gas mantles annually.

Thorium and its compounds are radio-active, and since monazite sand is plentiful it is proposed to prepare mesothorium to use instead of the rare and costly radium. Unfortunately mesothorium lasts only five or six years.

Germanium

This rare element was predicted by Mendeleef. Although the element is metallic, in its compounds it acts like a non-metal, resembling carbon. Of the two oxides, GeO and GeO_2, the lower is so weakly basic that salts are not numerous. The higher oxide is acidic. Among germanium compounds are GeH_4, $GeCl_4$, $GeHCl_3$ (germanium chloroform) and GeS.

CHAPTER XXXV

VANADIUM, MOLYBDENUM, TUNGSTEN AND URANIUM. RADIOACTIVITY

At the left of Group V of the periodic table are *vanadium*, *columbium* and *tantalum* and at the left of Group VI are *chromium*, *molybdenum*, *tungsten*, and *uranium*. The first three were called rare elements, but that adjective no longer applies to vanadium, which is now used in steel making. Chromium will be studied in connection with manganese.

VANADIUM

Vanadium. — Vanadium was first described as an element in 1830 by Sefstrom. It occurs everywhere in small amounts in the soil, but its chief ore is vanadinite, $Pb(VO_4)_2.PbCl_2$. The ashes of Peruvian coal contain as high as 48 per cent of vanadium pentoxide, V_2O_5. Peru has almost the only workable deposits of vanadium ore.

Preparation and Properties. — Pure vanadium is not easy to prepare. Its ores are reducible at high temperatures, but the free element combines with most reducing agents as well as with nitrogen. Reduction by "mixed metal" or by carbon in a vacuum furnace is the usual practice. The element is silvery white, very hard and rather brittle. It melts at 1720° and has a density of 6.02. When added to steel it makes the alloy harder and greatly increases its tensile strength. Ferrovanadium is easier to prepare than vanadium itself and is the form used in the steel industry. This alloy is made by heating a mixture of vanadium oxide or sulfide, iron filings and coke in an electric furnace (Fig. 112).

Compounds of Vanadium. — Vanadium exhibits valences of two, three, four and five in its compounds. There are four chlorides, VCl_2, VCl_3, VCl_4, and VCl_5. Vanadous sulfate, $VSO_4.7\ H_2O$, and vanadic sulfate, $V_2(SO_4)_3$, are both known. In fact, the latter forms a series of alums, such as $KV(SO_4)_2.12\ H_2O$. The sulfide, VS, and the pentoxide, V_2O_5, are familiar. The pentoxide is used as a catalyst in dye manufacture. The following table shows the similarity between vanadium and phosphorus:

Sodium orthophosphate, Na_3PO_4	Sodium orthovanadate, Na_3VO_4
Sodium metaphosphate, $NaPO_3$	Sodium metavanadate, $NaVO_3$
Sodium pyrophosphate, $Na_2P_4O_7$	Sodium pyrovanadate, $Na_2V_2O_7$

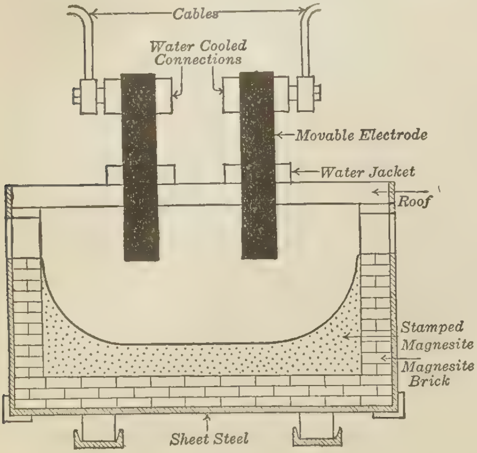


FIG. 112

Besides these, many complex compounds of vanadium exist. Vanadium salts are prepared from the ores much as chromium compounds are made from chromite. On fusion of the vanadium ore with sodium carbonate and a solid oxidizing agent, sodium vanadate, Na_3VO_4, is secured. To a solution of this salt an excess of ammonium chloride is added, producing a precipitate of ammonium metavanadate:

$$Na_3VO_4 + 3\ NH_4Cl \rightarrow NH_4VO_3 + 3\ NaCl + H_2O + 2\ NH_3.$$

The ammonium vanadate yields the pentoxide on ignition. This oxide is a starting point in the preparation of many compounds.

COLUMBIUM AND TANTALUM

Columbium and Tantalum. — Columbium was named in honor of its discovery in an American ore. It was first found in a Connecticut mineral, columbite, a ferrous metacolumbate, $Fe(CbO_3)_2$. Europe persists in calling it niobium. Columbium and tantalum occur together in columbite and tantalite, the name of the mineral depending on which element is found in the greater proportion. Samarskite contains both elements along with the rare earths.

Columbium is steel gray, about as hard as wrought iron, rather malleable and ductile. It melts at 1950° and has a density of

12.75. It unites with nitrogen and hydrogen at high temperatures, is attacked by fused alkalies, but resists the common acids rather well. Such compounds as $CbCl_3$, Cb_2O_5, $Mg_3(CbO_4)_2$, $Ca_2Cb_2O_7$, and many complex compounds are known.

Tantalum is a bright metal resembling platinum in appearance. It is so ductile that it may be drawn to very fine wire and since it also has a very high melting point, 2850°, it offers possibilities as an electric lamp filament. It was once used for this purpose, but the tungsten filaments are better. Tantalum resists alkalies and all acids except hydrofluoric. It has commercial possibilities. Such compounds as $TaCl_5$ and K_2TaF_7 have been prepared.

MOLYBDENUM

Molybdenum. — Molybdenum occurs chiefly as molybdenite, MoS_2, a black, lustrous mineral resembling graphite, but twice as heavy. Wulfenite, $PbMoO_4$, is also found. The ores need concentrating before smelting. Fortunately, the flotation process (page 426) is particularly suitable for the sulfide minerals. Colorado now leads in production, although Australia and Canada both produce considerable ore. The element is usually prepared by the Goldschmidt process or by reduction with "mixed metal." It is silvery white, melts at 2500° and has a density of 8.6. During the Great War, Germany was forced to substitute molybdenum for tungsten in high speed tool steel. Ferro-molybdenum, the form in which the element is added to steel, is prepared in the electric furnace by heating a mixture of molybdenum ore, coke and iron. As a tungsten substitute it is uncertain in behavior, so its success in that respect is still in the future. But steels carrying a very small proportion of molybdenum and some chromium possess remarkable tensile strength and are used for crank shafts, axles of busses and in airplane motors. Molybdenum itself can be tempered and forged like iron. Also like iron it takes up carbon when hot. The element finds some use in dental tooth plugs and in supports for tungsten filaments in lamps.

Molybdenum Compounds. — On roasting the sulfide, MoS_2, the *trioxide*, MoO_3, is formed. This is a yellow white powder which dissolves readily in sodium hydroxide with formation of *sodium molybdate*, Na_2MoO_4. If ammonium molybdate solution be poured into dilute nitric acid, *molybdic acid* is formed. This reagent is used to precipitate orthophosphates as the yellow precipitate $(NH_4)_3PO_4.12\,MoO_3.xH_2O$. This is the usual procedure in all analytical determinations of phosphorus. The composition of this yellow precipitate is so variable that it is more accurate to dissolve it in ammonium hydroxide and reprecipitate as $MgNH_4PO_4$, which is then dried and ignited to be weighed as $Mg_2P_2O_7$.

There are several oxides of molybdenum, Mo_2O_3, Mo_5O_{12}, Mo_2O_5, Mo_3O_8, MoO_2, MoO_3 and possibly others. MoO_3 and molybdic acid have such a tendency to unite that many complex salts like $Na_2Mo_{10}O_{31}.21\,H_2O$ are known.

Among the sulfides are Mo_2S_3, MoS_2, MoS_3 and MoS_4.

TUNGSTEN

Tungsten. — Tungsten was discovered by Scheele in "scheelite" or calcium tungstate in 1781 and is supposed to have been a constituent of the historic "Damascus blades" — unknown to the makers. The chief ore is ferrous manganese tungstate, $FeMnWO_4$, called wolframite. (The Germans insist on calling the element "wolfram" and all chemists agree on W as the symbol.) Before the war most of the ore came from China, but after this source of supply was shut off the price soared to 13 times the pre-war mark and production in California and Colorado was stimulated. In 1918, the United States produced over 4000 tons of tungsten. After the war prices fell and the easily-mined Chinese ores once more led in the world's markets.

Wolframite is fused with sodium carbonate and the sodium tungstate, $Na_2WO_4.2\,H_2O$, formed extracted with hot water. When this salt is treated with acids the free tungstic acid, $H_2WO_4.H_2O$, is precipitated. On ignition the oxide, WO_3, is secured. This oxide may be reduced by carbon or by the Goldschmidt process, but most of it is reduced by hydrogen in an electrically heated furnace at 1000°, or above.

Properties. — Tungsten has the highest melting point of all the metals, 3350°. Only carbon has a higher melting point, but carbon at high temperatures has a greater vapor pressure than tungsten. Tungsten is steel-gray, very hard and very heavy with a density of 18.64. The metal is obtained as a powder on reduction of the oxide and must be worked into strong filaments or rods. This was a great problem. Melting (at 3350°) is not practicable and moreover the melted product becomes brittle when cold. It has been found that the only way to secure strong compact tungsten is to work it while very hot, but not melted. The reduced powder is compressed to brittle bars which are heated by electric resistance furnaces in a reducing atmosphere of hydrogen to about 1500°. The bars are taken out, smoking in the air, and worked in a swaging machine, which draws them down gradually to smaller and smaller rods. With repeated heating and working, the metal becomes stronger and more malleable. If desired for sheet, it is hammered and rolled, but if desired for wire it is drawn finer and finer until it is strong enough to be pulled through diamond dies to the diameter needed for lamp filaments. It is usual to draw it through 100 dies, each a shade smaller than the previous one. In many respects tungsten is superior to steel. It never rusts and is not attacked by acids except slightly by citric.

Tungsten lamp filaments are saving the people of this country a few hundred million dollars each year. The old carbon filaments used 3.25 watts per candle power, while the modern tungsten lamp uses but 1.25 watts for the same illumination. We use 166,000,000 of these lamps annually.

High speed steel cutting tools contain 14–25 per cent tungsten. Since these tools can be worked on the lathe until red hot without losing the necessary hardness, their use means an enormous saving in machine shop expense. Cady observes that one man at a lathe with tungsten steel tools can do the work formerly done by five men with five tools at five lathes. He also believes that high speed tools have reduced the cost of automobiles considerably. And yet it is not long since tungsten was a "rare" element!

Tungsten Compounds. — There are four chlorides, WCl_2, WCl_4, WCl_5 and WCl_6. The hexachloride is formed by passing chlorine over tungsten at 300°. The others are secured by reduction of the hexachloride. The most important oxides are WO_2 and WO_3. Sodium tungstate, Na_2WO_4, is the best known salt. It is used in dyeing and in fireproofing fabrics and in making X-ray screens. Many complex tungstates are known. The many colored "tungsten bronzes" contain less oxygen than the tungstates. They are used as pigments. Phosphotungstic acid, $H_3PO_4.12\,WO_3$.-

$18\ H_2O$, is a reagent for alkaloids and protein with which it gives characteristic precipitates. Other complex acids of this type have been prepared.

URANIUM

Uranium. — Pitchblende, mainly uranium oxide, U_3O_8, with a little of many other elements present, is a uranium ore found in Bohemia and Cornwall. Carnotite, a uranate and vanadate of potassium, $K_2O.2\ UO_3.V_2O_5.3\ H_2O$, is found in Utah and Colorado. Cleveite, found in Norway, contains uranium and a number of rare elements. It was in this mineral that Ramsay first discovered helium. Samarskite is a complex tantalo-columbate of uranium, yttrium, iron, and other elements. Klaproth first discovered uranium (1889) in pitchblende.

Uranium is a white metal, melting at about 1500°. Its density of 18.68 ranks it as one of the heaviest elements. It slowly oxidizes in the air and dissolves in the common acids. The element is prepared by reduction of the oxides with carbon in the electric furnace. Uranium was used as one of the catalysts in the Haber process of making ammonia.

Uranium Compounds. — There are two oxides, UO_2 and U_3O_8, and four chlorides, UCl_3, UCl_4, UCl_5 and UCl_6. There are few salts in which uranium alone takes the place of hydrogen of acids. Usually the uranyl group (UO_2) acts as the positive radical. Uranyl nitrate, $UO_2(NO_3)_2.3\ H_2O$, and uranyl sulfate, $UO_2SO_4.3\ H_2O$, are beautiful yellowish crystalline salts. The element is acid-forming like chromium in such compounds as $K_2U_2O_7$ (like $K_2Cr_2O_7$). Uranium compounds are used in making a yellow-green fluorescent glass. When pitchblende is roasted with lime, calcium uranate, $CaUO_4$, is formed. With sulfuric acid this yields uranyl sulfate, UO_2SO_4, which with excess sodium carbonate becomes sodium uranate, Na_2UO_4. Acidified, it yields the diuranate, $Na_2U_2O_7$, just as the chromates change to dichromates.

RADIOACTIVITY

The Crookes Tube. — About 1878 Sir William Crookes discovered that high-vacuum tubes conducted electricity. He made these tubes in a variety of shapes, but the essential features are shown in the accompanying drawing (Fig. 113). Sealed-in wires at *A* and *C* support the anode and cathode. Crookes observed that some peculiar radiations from the cathode, "cathode rays," caused a yellowish green fluorescence where they hit the glass wall of the tube at *B*. Shields of heavy metal were sometimes placed in the path of these rays and caused corresponding shadows on the fluorescent surface of the glass. A magnet deflected the rays.

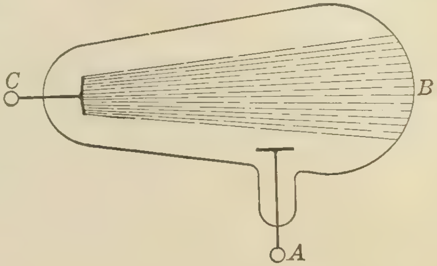
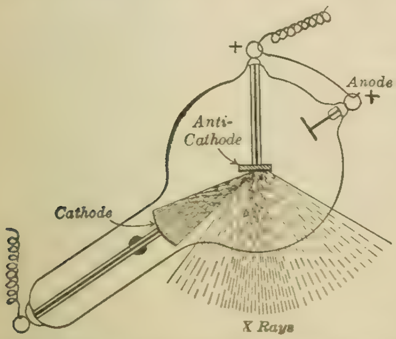


FIG. 113

X-rays. — Röntgen, in 1895, observed mysterious radiations, "X-rays," proceeding from Crookes tubes and penetrating supposedly opaque substances such as paper, wood, flesh and fabrics. These rays were secondary, that is, they were started by the impact of cathode rays on glass or other substance in their path. The fact that bones, metals and certain other substances were opaque to the X-rays made possible photographs of great use. For example, a needle or bullet could be located in the flesh. Figure 114 represents a modern X-ray bulb.



Reprinted, by permission, from Black and Conant's *Practical Chemistry*, The Macmillan Co.

FIG. 114

Becquerel Rays. — Henri Becquerel in 1896 conceived the idea that perhaps any fluorescent or phosphorescent substance might be a source of similar penetrating rays. He wrapped photographic plates in black paper and laid on them many such substances. Only one, potassium uranyl sulfate, $K_2UO_2(SO_4)_2$, produced any effect on the photographic plate. From this beginning Becquerel proceeded to show that any uranium compound gave off these penetrating "Becquerel rays" and that they discharged the leaves of an electroscope

(Fig. 115). Later, Rutherford showed that this was due to ionization of air molecules surrounding the leaves.

Radium. — Because of Becquerel's work with the penetrating radiations from uranium compounds the Curies (Madame Marie and her husband, Professor Pierre Curie of the Sorbonne) decided to examine some of the residues from pitchblende, a uranium mineral found in Bohemia. After careful work they found that the barium chloride obtained from this ore gave off more powerful radiations than the ore itself. This led them to decide that the barium chloride dragged with it the mysterious substance responsible for all the radiations. By painstaking work they separated a material which had millions of times the radiating power of the pitchblende. This was radium chloride. In 1910 Madame Curie completed her brilliant work by isolating the element radium. She electrolyzed an aqueous solution of radium bromide, using a mercury cathode. The radium deposited in the mercury was secured by distilling off the latter metal. The radium prepared looked like metallic calcium or barium and acted like them. It quickly tarnished in the air and decomposed water at a moderate speed. Its carbonate and sulfate were insoluble and its hydroxide a moderately strong base. In short, radium so completely resembled barium, calcium and strontium in properties that it had to be placed in Group II of the periodic table. Its valence is 2.

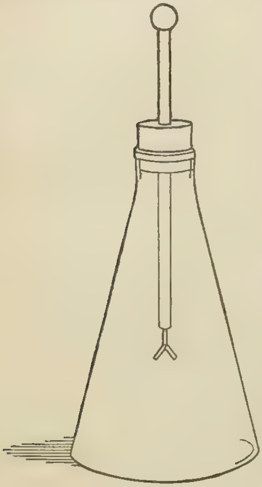


Fig. 115

To find the exact atomic weight of radium was a simple matter, when it was known to be bivalent. Analysis of the chloride showed the proportion by weight of chlorine and radium to be 35.46 : 113; therefore, the formula must be $RaCl_2$ and the atomic weight of radium 226.

Radium Rays. — It was soon developed after the discovery of radium that it gives off three types of radiations. The ***alpha rays*** are positively charged atoms of helium moving 18,000 miles per second. They do not actually travel 18,000 miles, however, in any time; they are stopped completely before they have gone 8 cm. through the surrounding air. After colliding with several thousand air molecules their initial velocity is reduced to nothing. But they produce very appreciable effects while traveling. Much heat is developed and as they smash through air molecules some of the latter have electrons knocked out of them and thus become ionized particles. Now ionized gas molecules act as nuclei for the condensation of moisture just as well as do dust particles. C. T. R. Wilson showed this very cleverly by placing a bit of radium in a bulb of air saturated with water vapor. On sudden cooling, the drops of moisture condensed as fog wherever ionized air molecules existed. Wilson photographed these fog tracks, thus showing the path of an alpha particle. This experiment furnished convincing evidence of the existence of atoms and molecules.

The collision between an alpha particle and a crystal of zinc sulfide is marked by a visible flash of light. The ***spinthariscope*** (Fig. 116) is a simple contrivance for magnifying this effect. At one end of a small tube is a zinc sulfide screen and near this is a minute speck of a radium salt. At the other end of the tube is a lens to magnify the flash of light when an alpha particle hits the screen. The human eye needs fifteen or twenty minutes of rest in darkness before it is possible to observe the faint flashes of light. It is decidedly impressive to see the work of a single atom and to realize that this bombardment continues for thousands of years. These alpha rays are able to decompose water, to convert oxygen into ozone, and to bring about the union of hydrogen and chlorine.

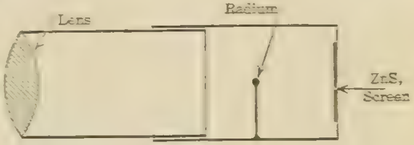


FIG. 116

The ***beta rays*** are identical with cathode rays, but move faster and are 100 times as penetrating. These cathode radiations and beta rays are known to be merely streams of electrons. When thrown off by radium they move 180,000 miles per second (the velocity of light). Since they have only 1/7000 the mass of alpha particles, they are deflected much more by a magnetic field (Fig. 117). As negative particles they are deflected in the opposite direction from alpha particles. In spite of their tremendous initial velocity, they are lost after smashing through a few cm.

of air. In a vacuum tube there is but slight opposition to their movement.

The *gamma rays* resemble X-rays but are far more penetrating. They are a wave motion of the ether, not streams of small particles, and hence are not deflected in a magnetic field. Alpha particles are stopped by 0.1 mm. thickness of aluminum foil, beta rays by 1 cm. thickness, and gamma rays by 1 foot of iron.

The Disintegration of Radium. — Rutherford (then at McGill University) was the first to suggest (1902) that radium actually breaks down by throwing off other elements at great velocity. Ramsay and Soddy proved that the alpha particles are atoms of helium. Rutherford later secured a gas from radium which he condensed by cooling in liquid air and volatilized on warming. This peculiar gas was itself radioactive, although this activity disappeared in less than a week. It was called "radium emanation" until Ramsay, working with a few cubic millimeters, determined its molecular weight (222.4) and named it *niton*.

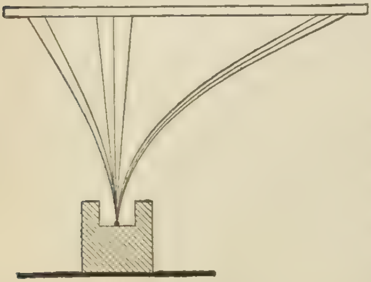


Fig. 117

A series of disintegration products has been discovered starting with uranium and, by twelve intermediate products, ending with lead. Since all uranium compounds or minerals are radioactive, they must contain radium. By measuring the amount of helium released from a given weight of radium, we have learned that one half of a given specimen of radium must decay in about 1850 years (the "half life" of the element). If all the radium associated with a uranium salt be removed, the remaining salt gradually recovers its activity; that is, more radium is formed from the uranium. Thus there is a definite ratio of radium to uranium in any uranium ore, resulting from a balance between the rate of formation and rate of decay of radium. All the radium in the world to-day is younger than the human race.

This conception of radium seems to shake our definition of an element, but it need not. We are unable to start, stop, hasten or retard this disintegration. In liquid air or the electric furnace, radium calmly goes on the even tenor of its way, supremely indifferent to the frantic efforts of mere human beings. So we rest on the conception of an element as a substance that cannot be decomposed by man. We give below the radium decay series as arranged by Alexander Smith (*College Chemistry*). "He" represents an escaping helium atom and "E" an electron. The average life and atomic weight of each element is given:

$U_1 \rightarrow He +$	$UX_1 \rightarrow E +$	$UX_2 \rightarrow E +$	$U_2 \rightarrow He +$	Ionium
8×10^9 y.	35.5 d.	1.65 m.	3×10^6y.	2×10^5y.
238.2	234.2	234.2	234.2	230.2
$\rightarrow He +$ Radium	$\rightarrow He +$ Niton	$\rightarrow He + Ra - A$	$\rightarrow He + Ra - B$	
2440 y.	5.55 d.	4.3 m.	38.5 m.	
222	222	218	214	
$\rightarrow E + Ra - C$	$\rightarrow E + Ra - C_1$	$\rightarrow He + Ra - D$	$\rightarrow E + Ra - E$	
28.1 m.	10^{-6} sec.	24 y.	7.2 d.	
214	214	210	210	
$\rightarrow E + Ra - F$	$\rightarrow He + Pb$ (end)			
196 d.				
210	206			

It is a startling fact that lead occurring in uranium ores has an atomic weight of 206, while common lead has an atomic weight of 207.2. To add to the novelty the atomic weight of lead associated with thorium (also radioactive) is 208.4. Remember that the weight of an electron is negligible, only 1/1700 that of a hydrogen atom, and that a helium atom has a weight of 4. Now check the weights in the uranium-radium-lead series above and it will be apparent that the final product, lead, must have an atomic weight of 206. Extremely accurate atomic weight determinations by Richards of Harvard gave the same result. These three forms of lead, with identical chemical properties and different atomic weights, are called *isotopes*.

Energy of Radium. — One gram of radium gives off more than enough heat to melt its own weight of ice every hour, to be exact, 134 cal. This heat is the result of the collisions of alpha and beta particles with surrounding substances. In changing to lead 1 cc. of niton gives off a total of 7,000,000 cal., but this heat is distributed over a long period of time. Many scientists now believe that there is enough radium in the earth to account for the present terrestrial temperature. When atoms unite with each other as in ordinary reactions, it is evident that only a minute fraction of the total energy locked up in the atoms is released. We may or may not find the key to this vast storehouse of energy.

Uses of Radium. — The chief use of radium to-day is as a therapeutic agent. Its radiations have a greater effect on unhealthy tissue than on normal tissue and so, if properly managed, it is possible to destroy cancerous tissue *on the surface* of the body. Some skin diseases are treated with radium, but there is still much dispute about its beneficial effects. However, it seems to be definitely established that many accessible cancers have been cured by careful use of sufficient radium. The emanation is much used in hospitals because it can be applied conveniently in small tubes and its use permits the radium itself to be locked up in a safe or applied to a particular case. More emanation is constantly being formed. The curative effect of some spring waters has been ascribed to radium emanation. Too long an exposure to any considerable quantity of radium causes dangerous burns, so the powerful material is kept in thick lead tubes. Glass tubes containing it develop a violet or brown color. Some gems are affected.

A luminous paint is prepared for *radiolite* watch faces, door numbers, etc., by mixing 10,000 parts of zinc sulfide with from 1 to 10 parts of a radium salt. The action is the same as in the spinthariscope.

The Radium Industry. — So far the world has prepared only 100–125 g. of radium (about 4 oz.) and there is not enough for the use of medical investigators. The price has varied from $100,000 to $120,000 per gram, but that does not discourage purchasers. The pitchblende deposits of Bohemia are nearly exhausted and the only important source of the metal to-day is the carnotite ore of Utah and Colorado. This does not occur in a concentrated form and when worked up by four months of careful labor yields only 2 mg. of radium per ton. For some years we exported carnotite ores to Germany without realizing what the Germans wanted it for — and bought back our own radium from them. Now at least two American companies are producing. From the medical standpoint, the use of radium on luminous watch faces is unfortunate, as the element so used is absolutely lost to the world. However, there is not more than twenty cents' worth of radium on a single watch.

Other Radioactive Elements. — ***Thorium*** decays and yields a series of active products. With 10 intermediate compounds it gives an end product of lead. The first product, mesothorium, is quite radioactive and, being far cheaper, is used as a substitute for radium. Unfortunately it lasts only 5.5 years.

Actinium is radioactive and, indeed, some of the more common elements exhibit slight activity.

CHAPTER XXXVI

CHROMIUM AND MANGANESE

Although chromium is found in the seventh group of the periodic table and manganese in the eighth, they have so many points in common that they should be studied together. Moreover, chromium has no great resemblance to the other members of its subgroup. These two elements are remarkable for the number of their oxidation stages and the great variety of their compounds. Their lower oxides are basic and their higher oxides acidic (compare with lead).

CHROMIUM

Occurrence. — Vauquelin first prepared the metal (1797) by making chromium oxide from the mineral crocoite, $PbCrO_4$, and reducing this oxide with carbon. The only important ore for commercial purposes is chromite, $Fe(CrO_2)_2$, which has already been mentioned as a spinel (see magnesium). It is mined in California, Rhodesia, Quebec, Siberia and New Caledonia. During 1916 the United States imported 114,655 tons, while California produced 47,000 tons.

Metallurgy and Properties. — The free element is not prepared in great quantity, as its alloy with iron is cheaper and more suitable for steel making. Most of this alloy, "ferrochrome," is made by carbon reduction of chromite in the electric furnace. A small amount of the carbon-free alloy is made by the Goldschmidt process. Ferrochrome, carrying 60 per cent of the metal, is added to special steels used for safes, armor plate, projectiles, autos and high-speed tools. It confers great strength on the steel. Some of the acid-proof alloys as well as "stainless steel" contain chromium. Three fourths of all American alloy steels contain chromium.

Chromium is a brilliant, silvery metal, hard and brittle. It melts at 1520° and has a density of 6.9. The powdered metal burns in oxygen with formation of the trioxide, Cr_2O_3. With chlorine it forms the chloride as it does with hydrochloric acid. In fact, it is easily attacked by cold concentrated or hot dilute hydrochloric and sulfuric acids. Yet nitric acid does not affect the metal.

The Passive State. — After chromium has been dipped in concentrated nitric acid it is not attacked by hydrochloric acid. The explanation is not clear. We cover our ignorance with a word and declare that the metal is in the "passive state." Some authorities insist this is due to a protecting film of oxide, but that scarcely explains why chromium made by the Goldschmidt process is passive. When two pieces of this metal, one passive and the other active, are dipped in an acid solution and connected by a wire, a difference of potential of 1.6 volts is found. The passive state is found with iron and a few other elements. If it were stable in the case of iron, it would give us a rust-proof structural metal and save the world countless millions.

OXIDATION AND REDUCTION REACTIONS OF CHROMIUM COMPOUNDS

Series of Chromium Salts. — As illustrations of the different series to which salts of chromium belong there are presented such salts as

$$CrSO_4 \text{ and } CrCl_2,$$

chromous sulfate and chromous chloride. These salts are evidently derived from a basic oxide, CrO, in which the element chromium is bivalent.

There is a second series of salts, illustrated by

$$Cr_2(SO_4)_3 \text{ and } CrCl_3,$$

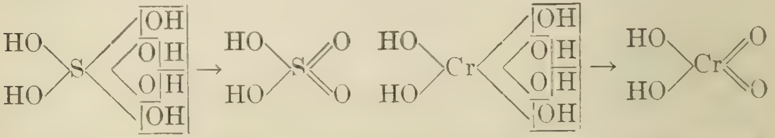
chromic sulfate and chromic chloride, derived from the basic oxide, Cr_2O_3, in which the valence of the element is three.

EXERCISE 1. — Write the equations showing how these four salts could be prepared by the action of the appropriate acids on oxides or hydroxides of chromium.

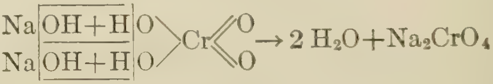
Quite different from the preceding are the salts of the series illustrated by

$$K_2CrO_4 \text{ and } Na_2CrO_4,$$

potassium chromate and sodium chromate. The oxide of chromium from which these salts are derived is represented by the formula CrO_3, in which chromium has a valence of six, like sulfur in sulfuric anhydride, SO_3. Like the latter also, this oxide of chromium acts as an acid anhydride and is known as "chromic anhydride." This particular oxide can be prepared in red crystals. It must be the anhydride of chromic acid, H_2CrO_4, just as SO_3 is the anhydride of sulfuric acid. Since the central element in each oxide has a valence of six, it is logical to consider the possible existence of acids in which all six valences are used to hold $-OH$ groups. Such acids are unstable and by instant loss of water form the partly dehydrated products we work with in the laboratory, H_2SO_4 and H_2CrO_4:



The student must keep clearly in mind that the mere presence of OH groups does not guarantee the formation of $\bar{O}H$ ions in water solution. Nearly all acids contain OH groups, but it is only the hydrogen that is split off in ionic form. This acidic ionization is illustrated in the following equation:



$$\begin{matrix}\text{Na}\,|\,\text{OH}+\text{H}\,|\,\text{O}\\ \text{Na}\,|\,\text{OH}+\text{H}\,|\,\text{O}\end{matrix}\!>\!\text{Cr}\!<\!\begin{matrix}\text{O}\\ \text{O}\end{matrix} \rightarrow 2\,H_2O+Na_2CrO_4$$

Lastly, there are such salts as:

$$K_2Cr_2O_7,$$

which may be written, $K_2O.2\,CrO_3$, somewhat like the salts of pyrosulfuric acid. The chromate, K_2CrO_4, could be written, $K_2O.CrO_3$. In $K_2Cr_2O_7$, the oxide of chromium is the same as in K_2CrO_4. Therefore, no new series is illustrated, but a new set of chromates, just as there are two sets of phosphates, ortha and meta, and two sets of sulfates derived from the ortho and pyro acids.

There are, therefore, three principal series of salts of chromium—chromous, chromic and chromates. Of these, the chromous salts are so easily oxidized to the chromic forms that they are with difficulty preserved, and may be omitted from the list.

1. Chromous salts, derived from CrO ; valence of chromium, 2.
2. Chromic salts, derived from Cr_2O_3; valence of chromium, 3.
3. Chromates, derived from CrO_3; valence of chromium, 6.

Transformations in the Chromium Series.—The name *chromium* refers to the various colors exhibited by its salts. The chromic salts are all green or violet, the chromates are yellow and the dichromates are red. It is, therefore, a simple visual matter to follow the transformation of one series of salts into the corresponding salts of the other series.

1. *Comparison of salts of trivalent chromium with salts of chromic acid.* — If sodium hydroxide be added to solutions of chromic salts and then to solutions of the heavy metals, the results are the same. Solutions of all the heavy metals, when thus treated with sodium hydroxide, have precipitated the insoluble hydroxides. It was so with aluminum, with tin and with zinc. When chromium sulfate is so treated, insoluble chromium hydroxide, $Cr(OH)_3$ — the corresponding base — is precipitated. But if sodium hydroxide be added to a solution of sodium chromate no precipitated chromium hydroxide is obtained. The solution remains clear yellow. The expected hydroxide, if it were possible, would be $Cr(OH)_6$ or its partly dehydrated derivative, H_2CrO_4, chromic acid. Needless to state, such an acid would react with the base to form sodium chromate, the original salt. Chromium with a valence of 3 is quite different from chromium with a valence of 6.

2. *Comparison of chromates and dichromates.* — Just as the difference between potassium sulfate, $K_2SO_4(K_2O.SO_3)$, and potassium disulfate or "pyrosulfate," $K_2S_2O_7(K_2O.2\ SO_3)$, is one molecule of potassium oxide, K_2O, which base may be added in one case or removed in the other — so it is with the chromates and dichromates. By changing the *relative* quantity of base or acid present, the transformation may be accomplished in either direction. The ratio of base to acid in the two forms is

Potassium chromate, $K_2O : CrO_3 = 1 : 1$,
Potassium dichromate, $K_2O : 2\ CrCO_3 = 1 : 2$.

Therefore, by adding base to the red dichromate, the yellow chromate is produced; and by adding acid to the yellow chromate, the red dichromate is the result. It is important to notice that in this transformation there is no change of valence and therefore no reducing agent or oxidizing agent is used.

3. *The reduction of a chromate to a chromic form:*

a. When a neutral reducing agent is used.

The reduction of a chromate must take place in the presence of an acid, so that both reducing agent and acid must be introduced. The question arises, How much of each must be used? If alcohol be used as the reducing agent, acid must be added for two reasons: 1st, to unite with the base in the chromate, e. g., with the potassium oxide, K_2O; and 2d, to unite with the base produced, Cr_2O_3. If the salt used is potassium dichromate, $K_2Cr_2O_7$, it is clearer to consider it as made up of a basic and an acidic oxide, thus: $K_2O.2\ CrO_3$. In order to reduce the 2 CrO_3 to the lower oxide, Cr_2O_3, *three* atoms of oxygen must be removed. Expressing, for simplicity, the alcohol used as equivalent in reducing power to 3 H_2 and counting the sulfuric acid required for the two bases, K_2O and Cr_2O_3, as four molecules, the equation for this will stand as follows:

$$K_2Cr_2O_7+3\ H_2+4\ H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+7\ H_2O.$$

Exercise 2. — Write the equation for the reduction of the yellow sodium chromate, Na_2CrO_4, by the use of neutral stannous chloride.

b. When the reducing agent is an acid.

In this case very little additional acid will be necessary — perhaps none at all. If the reducing agent used is sulfurous acid, to remove the three atoms of oxygen from 2 CrO_3 will involve three molecules of the sulfurous acid, which by complementary oxidation will produce three molecules of sulfuric acid. In the last equation, four molecules of sulfuric acid were required; therefore, the additional sulfuric acid in this case will be only one molecule. The equation will read as follows:

$$K_2Cr_2O_7+3\ H_2SO_3+H_2SO_4 \rightarrow K_2SO_4+Cr_2(SO_4)_3+4\ H_2O.$$

The Oxidation of Chromic Salts to Chromate Forms

This may be effected by oxidation in the presence of a base. One method is to fuse the chromic salt with solid potassium chlorate and potassium hydroxide.

If the salt used be chromium sulfate, $Cr_2(SO_4)_3$, it is best to consider it as made up of a basic and an acidic oxide, $Cr_2O_3.3\ SO_3$. In order to oxidize the chromic oxide to chromic anhydride,

$2\ CrO_3$, three atoms of oxygen must be added and some base. The base must be added for two purposes:

1st, to neutralize the acid present, $3\ SO_3$. If the base used be KOH, six molecules will be needed.

2d, to neutralize the acid newly produced by the oxidation process, $2\ CrO_3$. This will require four more molecules of KOH, making ten in all. The equation will therefore read as follows:

$$Cr_2(SO_4)_3 + 3O + 10\ KOH \rightarrow 3\ K_2SO_4 + 2\ K_2CrO_4 + 5\ H_2O.$$

In qualitative analysis it is usual to separate the hydroxides of chromium and iron by addition of sodium peroxide to the wet suspension. The method would apply as well to solutions of chromium and iron salts. By representing the above reaction in stages it will be easy to understand the qualitative procedure just mentioned. It is hardly necessary to state here that sodium peroxide or water furnishes both sodium hydroxide and active oxygen:

1st stage, $Cr_2(SO_4)_3 + 6NaOH \rightarrow 3Na_2SO_4 + 2Cr(OH)_3$,
2d stage, $2Cr(OH)_3 + 3O \rightarrow 2\ CrO_3 + 3H_2O$,
3d stage, $4NaOH + 2CrO_3 \rightarrow 2Na_2CrO_4 + 2H_2O$.
Summary, $Cr_2(SO_4)_3 + 3O + 10NaOH \rightarrow 3Na_2SO_4 + 2Na_2CrO_4 + 5H_2O$

Chromous Compounds. — When chromium is dissolved in hydrochloric acid it is ***chromous chloride***, $CrCl_2$, not chromic chloride, $CrCl_3$, that is secured. The active hydrogen released and the excess metal would reduce any chromic chloride to the lower form. Once having made this chromous salt, it is impossible to keep it. It is quickly oxidized by air and even by water. The only chromous compound of any stability at all is the acetate, which may be precipitated in dark red crystals by addition of sodium acetate to the solution of chromous chloride. Chromic chloride is readily reduced to the chromous state by zinc and hydrochloric acid or by stannous chloride. ***Chromous hydroxide***, $Cr(OH)_2$, is a yellow precipitate, while it lasts.

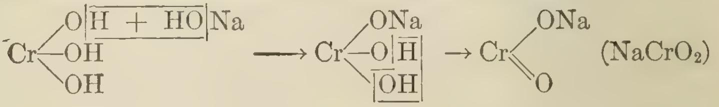
Chromic Compounds. — Anhydrous ***chromic chloride***, $CrCl_3$, is prepared by the action of chlorine on chromium. The beautiful lavender-colored leaves are quite insoluble in water, yet a trace of chromous chloride causes the insoluble chloride to dissolve completely. The ordinary form of chromic chloride is soluble.

It is easily made by reduction of a dichromate or of CrO_3 itself with alcohol in a solution of hydrochloric acid:

$$2\,CrO_3+6\,HCl+3\,C_2H_5OH \rightarrow 2\,CrCl_3+3\,C_2H_4O+6\,H_2O.$$

The aldehyde resulting from oxidation of the alcohol is volatile, so only the green solution of chromic chloride is left.

Chromic Hydroxide, $Cr(OH)_3$. — This hydroxide is a bluish-green amorphous precipitate when ammonium hydroxide is added to a solution of a chromic salt. The stronger bases could be used, but the hydroxide dissolves in an excess of sodium hydroxide. It is probable that the reaction proceeds as follows:



Chromic hydroxide also dissolves in acids, as it is amphoteric.

Chrome Alum, $KCr(SO_4)_2.12\,H_2O$. — This double salt is formed by mixing solutions of potassium sulfate and chromic sulfate, $Cr_2(SO_4)_3$, in molecular proportions. From the resulting solution large and beautiful ruby crystals are secured on slow evaporation.

Green and Violet Chromic Salt Solutions. — All chromic salt solutions are green after boiling, but on standing in the cold they turn violet. The former change in color is accompanied by the disappearance of the simple $\overset{+++}{Cr}$ ions. Cady states that the violet color is due to $\overset{+++}{Cr}$ ions and the green color to complex ions. Werner believes that around the central atoms, in $CrCl_3$ for example, there are six groups, part of which may be water of crystallization. In fact in the violet form, which yields all the usual ions, he assumes these six groups to be water. Thus the formula is $Cr(OH_2)_6.Cl_3$. But in the green form two of these six water molecules are replaced by chlorine atoms, leaving only one chlorine atom so attached that it is ionizable. The formula may be represented by

$$\left[Cr\begin{matrix}Cl_2\\(OH_2)_4\end{matrix}\right]Cl\ +\ 2\,H_2O.$$

His theory receives support from the fact that in the green solution only one third of the chlorine atoms can be precipitated quickly by silver nitrate. In addition the electrical conductivity is much less than that of the violet solution.

Chromates and Dichromates. — The mineral chromite is the starting point in the manufacture of chromates. Fused in the air with potassium hydroxide (possibly with addition of a solid oxidizing agent) chromite yields the *soluble* potassium chromate which on addition of acid is converted into the dichromate:

$$4\,\mathrm{Fe(CrO_2)_2}+7\,\mathrm{O_2}+16\,\mathrm{KOH} \rightarrow 2\,\mathrm{Fe_2O_3}+8\,\mathrm{H_2O}+8\,\mathrm{K_2CrO_4}.$$

Addition of concentrated sulfuric acid to a solid chromate, or dichromate, liberates chromic acid, H_2CrO_4, or dichromic acid, $H_2Cr_2O_7$, and promptly dehydrates it into the anhydride, CrO_3. This precipitates in red crystals which readily dissolve in water and rehydrate to the acid.

Since potassium dichromate is much more soluble hot than cold, it is easily purified by crystallization. The remarkable change in color from the yellow chromate solutions to the orange-red dichromate solutions on acidifying, with the reverse action on neutralizing with a base, may be explained by supposing that the $\overset{--}{\mathrm{CrO_4}}$ ions react with $\overset{+}{\mathrm{H}}$ ions to form $\overset{--}{\mathrm{Cr_2O_7}}$ ions and water. Both chromate and dichromate solutions may exhibit the following equilibrium condition, shifted one way or another:

$$2\,\overset{--}{\mathrm{CrO_4}}+2\,\overset{+}{\mathrm{H}} \leftrightarrows \overset{--}{\mathrm{Cr_2O_7}}+\mathrm{H_2O}.$$

Addition of an acid increases the concentration of H ions and drives the reaction to the right. Addition of a base uses up the $\overset{+}{\mathrm{H}}$ ions and drives the reaction to the left. Since both $\overset{--}{\mathrm{CrO_4}}$ and $\overset{--}{\mathrm{Cr_2O_7}}$ ions are present in a dichromate solution, addition of $\overset{++}{\mathrm{Pb}}$ ions must result in formation of the more insoluble of the two salts, lead chromate and lead dichromate. Lead chromate is extremely insoluble and is precipitated. It is a yellow pigment used in paints. Barium chromate is a yellow precipitate formed under similar conditions. Sodium dichromate is much used in the "chrome tanning" of hides. It is reduced in the hide to the trioxide (Cr_2O_3) which forms an insoluble compound of some sort with the hide material.

Tests. — Chromium compounds may be detected by conversion into chromic salts and addition of sodium peroxide to a little of the very concentrated solution. The soluble yellow sodium chromate formed is treated with a solution of a lead salt. Yellow lead chromate is precipitated. When a chromate or dichromate is acidified and shaken with a solution of hydrogen peroxide, blue perchromic acid, $HCrO_4$, is formed. It is very unstable in this solution, but if a layer of ether be present the blue compound dissolves in the ether on shaking and lasts for some time. This reaction may be used as a test for chromium or for hydrogen peroxide. Chromium is grouped, in analysis, with ferric iron and aluminum because of the insolubility of its hydroxide.

MANGANESE

Manganese is the only known member of its sub-group, but it is placed in the same column of the periodic table with the halogens. It resembles the halogen family very little, although Mn_2O_7 corresponds to Cl_2O_7 and $HMnO_4$ to $HClO_4$.

There are five series of manganese compounds, each with a different valence of the metal. With each valence manganese seems to belong to a different group of elements.

A comparison follows:

OXIDE	VALENCE	RESEMBLES	COMMENT
MnO	2	Mg	Carbonates and sulfides exist; little hydrolysis of salts.
Mn_2O_3	3	Cr, Fe	Salts completely hydrolyzed.
MnO_2	4	Pb, Sn	Alkali manganites, strongly hydrolyzed.
MnO_3	6	S in sulfates	Manganates much more easily hydrolyzed than sulfates.
Mn_2O_7	7	Cl in perchlorates	Salts not hydrolyzed.

The list of oxides in the above table is not complete, but Mn_3O_4 is omitted because it is not a simple oxide; rather, it resembles Pb_3O_4. The fourth oxide listed, MnO_3, is very unstable, but it has been made. All the stable oxides tend to give off oxygen and form manganous salts when treated with acid. If the acid is oxidizable, like hydrochloric, chlorine is released (except when MnO is used). Heated in the air with strong bases, these oxides tend to take up oxygen and yield derivatives of the two highest oxides.

Occurrence. — The chief manganese ore is pyrolusite, MnO_2, mined in Russia and Brazil. Some manganese carbonate is mined in Montana. When our imports were cut off during the Great War other manganese deposits were mined. There were extensive workings within the city limits of Butte, Montana, but with the coming of peace it no longer paid to work such inferior ores.

Metallurgy. — Manganese compounds were long confused with iron compounds, but in the latter part of the eighteenth century the difference was recognized. Gahn first isolated the element. It is rather difficult to prepare pure manganese because, where the oxides are reduced with carbon in the electric furnace or blast furnace, some carbon unites with the metal. The pure element is prepared by Goldschmidt's method. Commercially the metal is of value mainly in the form of an alloy with iron. Such an alloy carrying less than 20 per cent manganese is called spiegeleisen, while an alloy carrying from 20 to 90 per cent is called ferromanganese. These alloys are added to steel to give it hardness and strength. A manganese steel carrying 11–14 per cent manganese, to mention an extreme case, is too hard to be machined and must be cast and ground to shape. Burglar-proof safes and armor plate are made of manganese steel.

Properties. — Manganese is a reddish-gray metal melting at 1260° and boiling at 1900°. It has a density of 7.2. It is very brittle and hard enough to scratch glass. In the air it is not tarnished, but acids as weak as acetic attack it; forming manganous salts. Heated to 1200° in a stream of nitrogen, it burns to the nitride.

Series of Manganese Salts. — The best way to compare the salts of manganese with those of chromium is to list the salt-producing oxides. These are:

1. Manganous salts,	derived from MnO;	valence of manganese, 2.
2. Manganic salts,	derived from Mn_2O_3;	valence of manganese, 3.
3. Manganates,	derived from MnO_3;	valence of manganese, 6.
4. Permanganates,	derived from Mn_2O_7;	valence of manganese, 7.

Illustrations of such salts are, in order, manganous sulfate, $MnSO_4$, manganic sulfate, $Mn_2(SO_4)_3$, potassium manganate, K_2MnO_4, and potassium permanganate, $KMnO_4$. Under chromium, the valences 3 and 6 were important. Manganese salts differ from those of chromium, 1st, in the existence of the permanganates; 2d, in the instability of the manganates and the consequent nonexistence of the salts, which would correspond to the dichromates; 3d, in the stability and importance of the manganous salts and the instability of the manganic salts. In short, the series resembles that of chromium, the difference being in the importance of, or emphasis placed on, the valences 2 and 7.

TRANSFORMATION IN THE MANGANESE SERIES

Although there are three important series of manganese salts, the transformations are easy to follow from the colors:

Manganous salts are pink,
Manganates are green,
Permanganates are purple.

All the stable oxides tend to give off oxygen and form manganous salts when treated with acid. If the acid is oxidizable, as hydrochloric, chlorine is released (except where MnO is used). Thus such salts as manganous chloride, $MnCl_2$, and manganous sulfate, $MnSO_4$, are formed:

$$MnO_2 + 4\ HCl \rightarrow 2\ H_2O + MnCl_2 + Cl_2$$
$$MnO + 2\ HCl \rightarrow H_2O + MnCl_2.$$

If manganous salts are oxidized in the presence of a base, manganese assumes the valence of 6 (as in MnO_3) and manganates are produced, exactly as was true in the case of chromium. This is illustrated as follows:

$$MnCl_2 + O_2 + 4\ NaOH \rightarrow 2\ NaCl + Na_2MnO_4 + 2\ H_2O.$$

This is equivalent to stating that any oxides of manganese heated in the air with a strong base tend to take up oxygen and yield derivatives of the two highest oxides.

The manganates are very unstable, differing from the chromates in this respect, tending to break down to manganese dioxide:

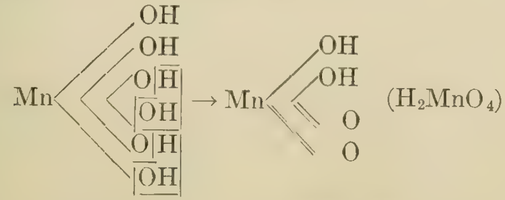
$$2\ K_2MnO_4 \rightarrow 2\ K_2O + 2\ MnO_2 + O_2.$$

Naturally, this action takes place more rapidly if acid be present to take up the alkali, K_2O, and thus start the decomposition. Even the weak carbonic acid of the air is sufficient to precipitate the brown oxide from the green manganate solution. On the introduction of any dilute acid into such solutions, the nascent oxygen released helps oxidize other molecules of the manganate into the permanganate:

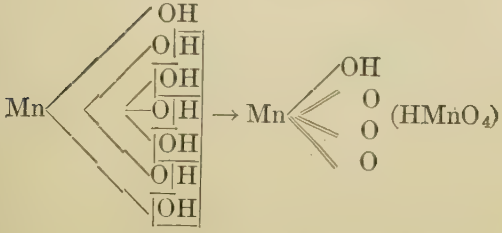
$$KMnO_4+CO_2 \rightarrow K_2CO_3+MnO_2+O,$$
$$2\ K_2MnO_4+O+CO_2 \rightarrow 2\ KMnO_4+K_2CO_3.$$

Thus the green manganate solution changes into the purple permanganate. In the manufacture of the latter substance, black manganese dioxide is fused with potassium hydroxide and potassium chlorate. The fused mass is dissolved in water, forming a green manganate solution, which is then transformed by carbonic acid, changing rapidly to a purple color, with precipitation of a brown hydrated dioxide, $MnO_2.2\ H_2O$. The permanganate is crystallized from the solution, after filtering, and the precipitated dioxide put through the process again.

If we consider all oxygen acids as hydroxides of the non-metallic element, the structure of manganic and permanganic acids is easily represented. The anhydride of manganic acid is MnO_3 ($H_2MnO_4 \rightarrow H_2O+MnO_3$), and therefore the valence of the manganese is 6. A mother acid, $Mn(OH)_6$, may be imagined. It is too unstable to be isolated. By the same logic permanganic acid should be derived from a mother acid, $Mn(OH)_7$.



Mother acid → manganic acid



Mother acid → permanganic acid

The Reduction of Potassium Permanganate. — Potassium permanganate is very commonly used as a strong oxidizing agent. The organic matter in drinking water is oxidized completely by boiling the water after the addition of a very dilute solution of this substance. The reduction of the permanganate amounts in effect to dropping from the oxide Mn_2O_7, to one of the lower oxides, MnO_2, MnO_3 and MnO. The extent of the reduction, and the answer to the question which oxide will be formed, is determined by whether the reduction takes place in basic, neutral or acid solution. If in basic solution, the oxide formed will be the one which acts acidic, MnO_3. In neutral solution manganese dioxide is formed; and in acid solution, the lowest oxide, which acts most strongly basic. The extent of the reduction differs in the three cases.

1. *Reduction in the presence of base.* — The only acidic oxide below permanganic anhydride is manganic anhydride, MnO_3. The reduction is effected by removal of only one atom of oxygen. If alcohol be used as the reducing agent and this is represented by its equivalent, H_2, the equation may be written thus:

$$2\,KMnO_4\ (\text{or } K_2O.Mn_2O_7)+K_2O+H_2 \rightarrow H_2O+2\,K_2MnO_4\ (\text{or } 2\text{-}K_2O.2\,MnO_3).$$

The purple permanganate is thus transformed in alkaline solution to the green manganate. With some excess of reducing agent the green manganate breaks down, yielding the brown manganese dioxide.

2. *Reduction in neutral solution.* — In a neutral solution, a neutral reducing agent such as alcohol will be oxidized by the atoms of oxygen with formation of manganese dioxide, which combines with neither acid nor base directly. This reduction is shown in the equation:

$$2\,KMnO_4+3\,H_2 \rightarrow K_2O+3\,H_2O+2\,MnO_2.$$

Thus, on warming with alcohol, the purple solution loses all color and the brown hydrated manganese dioxide, $MnO_2.2\,H_2O$, is precipitated.

3. *Reduction in the presence of an acid.* — If to a solution of a permanganate, sulfurous acid be added, the manganese is reduced to a valence of 2, to MnO; five atoms of oxygen are removed by the sulfurous acid and five molecules of sulfuric acid

are produced by the reciprocal oxidation. This acid produced is useful in removing the base present, K_2O, and then in removing the base produced, 2 MnO. The equations may be given in detail and summarized as follows:

(1) $2KMnO_4 \text{ (or } K_2O.Mn_2O_7) + 5H_2SO_3 \rightarrow K_2O + 2MnO + 5H_2SO_4,$
(2) $K_2O + H_2SO_4 \rightarrow K_2SO_4 + H_2O,$
(3) $\underline{2MnO + 2H_2SO_4 \rightarrow 2MnSO_4 + 2H_2O,}$
(4) Summary: $2KMnO_4 + 5H_2SO_3 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 2H_2SO_4$

Manganous Compounds. — Freshly precipitated manganous hydroxide, $Mn(OH)_2$, is of about the same order of solubility as magnesium hydroxide. Consequently ammonium salts dissolve it just as they dissolve the latter hydroxide. It is all a matter of decrease in $\overset{-}{OH}$ ion concentration, due to the formation of weakly ionized ammonium hydroxide.

Exercise 3. — Review magnesium hydroxide and then write the equations for the solution of manganous hydroxide by ammonium salts.

Manganese sulfide is the most soluble sulfide of the heavy metals. It is not precipitated by hydrogen sulfide unless a base or considerable sodium acetate be added. In the usual system of qualitative analysis, this pink sulfide is precipitated by ammonium sulfide. It oxidizes so readily in the air to the soluble manganous sulfate, $MnSO_4$, that analysts are accustomed to wash it with hydrogen sulfide water.

Manganic Compounds. — Manganese dioxide, MnO_2, is by far the most important compound of manganese. The mineral form is used in dry batteries as a depolarizer. Glass is usually decolorized by addition of manganese dioxide. Ferromanganese is made from the dioxide, which is also used to make dryers for paints. It is so very weak a base or acid that it is almost in a class by itself. Yet with cold concentrated hydrochloric acid it forms manganese tetrachloride, $MnCl_4$. On warming this gives off chlorine. (Equations?) On dilution it is hydrolyzed like lead tetrachloride, $PbCl_4$, to the dioxide. (Diagram this action.)

Manganese tetrahydroxide, $Mn(OH)_4$, is a weak acid forming salts like the manganites ($CaMn_2O_5$), which are strongly hydrolyzed. The calcium salt may be prepared as follows:

$$Ca(OH)_2 + 2\,Mn(OH)_2 + O_2 \rightarrow CaMn_2O_5 + 3\,H_2O.$$

Tests. — It is easy to recognize manganese compounds by melting them with potassium hydroxide and a little potassium nitrate or chlorate. The green color of the manganate formed is characteristic. A few drops of a solution of a manganese salt may be boiled with nitric acid and a little lead peroxide added (while holding the tube over a waste jar). On settling, pink permanganic acid may be seen. Both tests are remarkably delicate.

CHAPTER XXXVII

IRON, COBALT, AND NICKEL

	Atomic Weight	Density	Melting Point	Oxides
Iron	55.84	7.8	1510°	FeO, Fe_2O_3, Fe_3O_4
Cobalt	58.97	8.5	1478°	CoO, Co_2O_3, Co_3O_4
Nickel	58.68	8.8	1452°	NiO, Ni_2O_3, Ni_3O_4

These three elements occupy a position in the periodic table following manganese, somewhat as a bridge between two octaves or periods of the table. Their valence might be expected to reach 8, but each of the three elements displays valences of 2, 3 and 4. However, in nickel carbonyl, $Ni(CO)_4$, and iron carbonyl, $Fe(CO)_4$, there is some suggestion of a valence of 8. There is no vertical column relation between these three elements (as in the halogens). Rather, they occupy the position of a single element. They are all magnetic, all have high melting points, and all decompose water at high temperatures.

IRON

Occurrence. — Free iron in nature is rare. A little occurs in Greenland and a little is found in meteorites. These star fragments are largely iron mixed with 3–8 per cent nickel and sometimes a little cobalt. The most important iron ores are oxides, although the English ore is a carbonate. Iron pyrites, FeS_2, is mined as a source of sulfur rather than of iron. Hematite, Fe_2O_3, furnishes the world with, by far, the greater part of its iron. Limonite, $2\,Fe_2O_3.3\,H_2O$, is a yellowish ore, while magnetite, Fe_3O_4, is a black oxide. In addition to the workable ore beds there are iron oxides in clays to add to the beauty of coloring so conspicuous in Yellowstone Park and elsewhere. Bricks owe their colors to such oxides. Without the iron compound in the chlorophyll of green leaves vegetation wouldn't amount to much.

Without the iron compound known as hæmoglobin the blood could not function properly.

The United States is the most fortunate country in the world in the richness of iron ore deposits. Before the war, Germany was second and England third, but with the winning of Lorraine, France has taken from Germany her largest ore beds and now is second only to the United States in the richness of her iron ore deposits. Sweden has important ore beds, as has also Russia. China is rich in iron, but the industry is only in its infancy there. Canada mines and smelts a good deal of iron ore.

Metallurgy. — Carbonates of iron are converted into oxides on roasting, and oxides are reduced by heating in contact with coke and limestone. The raw materials are used in such enormous quantities that the location of steel cities like Pittsburgh and Gary depends upon relative freight costs. Consult the map showing the location of the great coal and iron ore beds as well as the concentration of population. Pittsburgh is on the edge of the greatest coke territory in the United States, so only the ore need be brought to her furnaces. It might be argued that it would cost less to haul the coke to the ore beds in Minnesota, but the manufacturer must consider the freight haul on his finished product. Pittsburgh is in the densely populated East. Limestone is so common that it is easily obtained in most states. Birmingham has ore, coal and limestone within easy reach, but is far from the greatest markets. Gary was built to take advantage of cheap water freight for ore from the Lake Superior region, while near the railroad center of the country and not too far from fuel. The marvelously cheap freight rates on the Great Lakes have a vital influence on the location of steel centers. Huge ore boats carry 13,000 tons of ore at a load, at a cost of about one sixth that by rail.

The greatest ore bed in the world is found around the western end of Lake Superior. A large deposit occurs in Alabama, another in New York, another in Colorado and several in California. California lacks coal, but is rich in fuel oil and water power. By a combination of electric furnace heat and the reducing action of fuel oil this state may yet succeed in smelting her enormous deposits of iron ore.

The Blast Furnace. — Iron was made many centuries ago, but its manufacture on a vast scale did not become possible until

1735 when coal was first used as the reducing agent. Yet during the first half of the last century charcoal was still in common use in American blast furnaces.

The modern blast furnace is of giant proportions (Fig. 118). Most of them are 90 ft. high and some have even reached a height

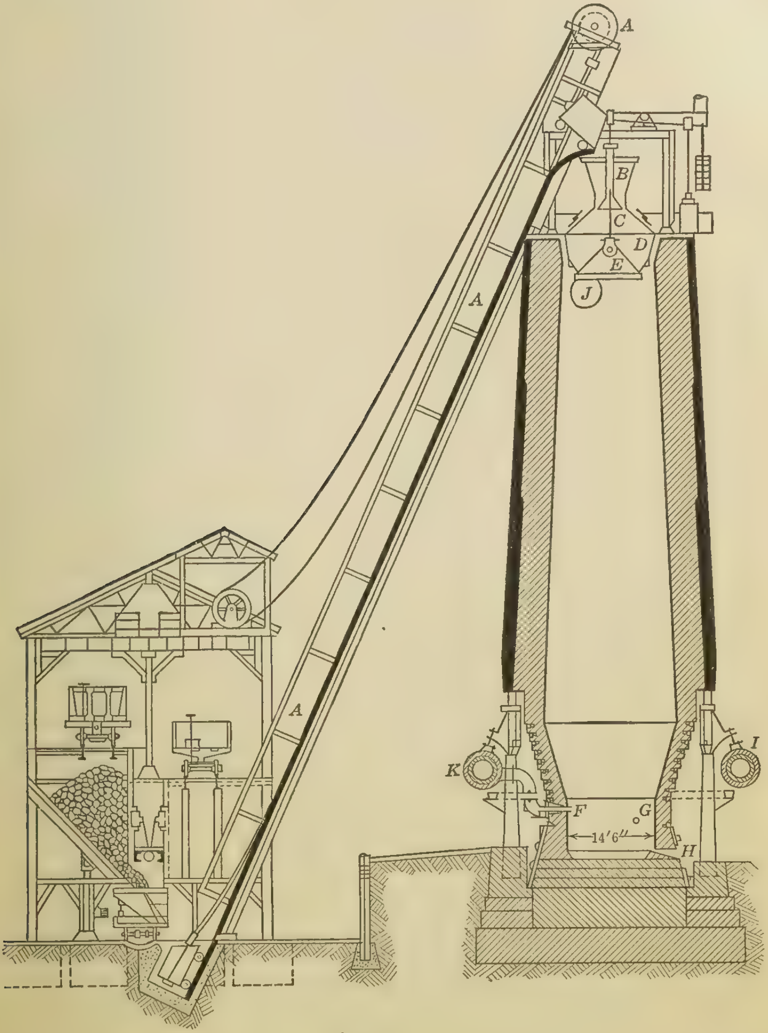


FIG. 118

of 125 ft. The greatest diameter is usually about 20 ft. They are built of heavy steel plates lined with fire brick. The lower part where the heat is more intense is usually bound with water-cooled bronze blocks set in the brick wall. At the top of the "stack," as the furnace is called, are double bell-shaped doors which admit the ore, coke and limestone without undue loss of gases. Below this point the stack steadily widens to allow for expansion of the charge. But at a certain point fusion of part of the material causes such a great decrease in volume that the stack tapers in accordingly. Otherwise the heavy charge would fall and burst the furnace. No doubt the correct angle of taper was learned by costly experience. The narrowing part is called the "bosh." Just below this is the "crucible" in which molten iron and slag accumulate. The tap hole for iron is at the bottom, but the "cinder notch" for the slag is a little higher. Just above the crucible are several openings called "tuyères," through which a great blast of heated air is blown to burn the coke. From 35,000 to 60,000 cubic feet of air per minute is required.

It may seem that hot carbon is the active reducing agent in the blast furnace, but the carbon monoxide formed is even more effective because it is a gas and hence comes in better contact with the ore. As the charge enters the stack, it soon reaches a temperature of 300°–400° and as it settles to lower and hotter zones the reducing action of carbon monoxide (exothermic) becomes effective. At still lower zones and higher temperatures the limestone loses carbon dioxide and becomes calcium oxide, which unites with the alumina and silica of the ore to form a fusible slag. At this point the hot coke adds its reducing action (endothermic). The pasty particles of free iron do not melt until they have dissolved enough impurities such as sulfur, silica and carbon to lower the melting point sufficiently. The melted iron runs in the crucible, while the lighter fluid slag floats on top (Fig. 119). The equations representing the various reactions follow:

$$C+O_2 \rightarrow CO_2$$
$$CO_2+C \rightarrow 2\,CO$$
$$Fe_2O_3+3\,CO \rightarrow 3\,CO_2+2\,Fe$$
$$Fe_2O_3+3\,C \rightarrow 3\,CO_2+2\,Fe$$

The iron is tapped off every 6 hours, but the slag is removed more frequently. The iron is run into molds from which the solid "pigs" are removed or it may be carried in great ladles to the steel mill without solidifying. Slag is carried away in ladles to the dump or is granulated by pouring into water. In this form it is easy to handle as railroad ballast or as a raw material for Portland cement. Since it is a complex calcium aluminum silicate it needs only to be burned with more lime and ground to produce a very fair grade of hydraulic cement.

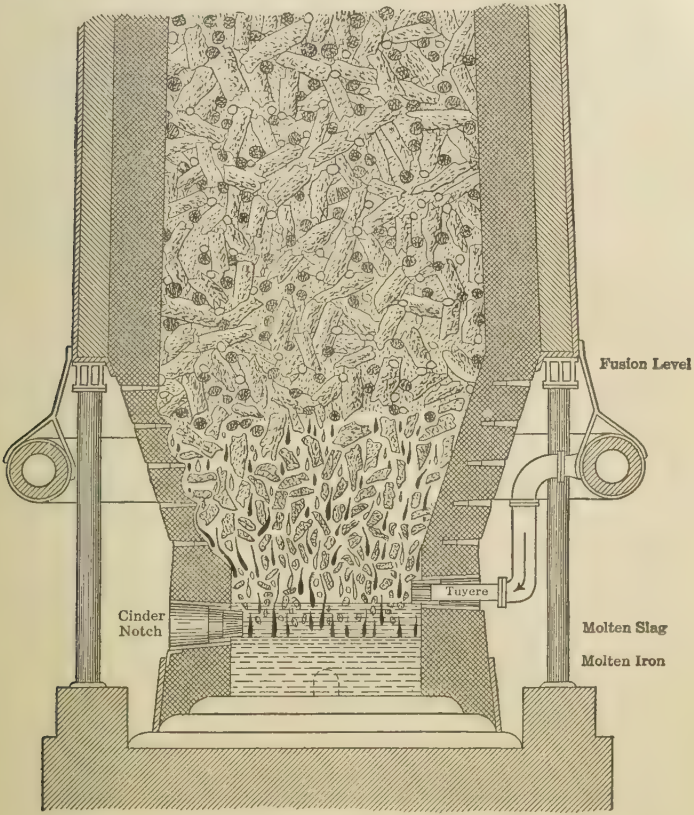


FIG. 119

A great deal of fuel is wasted because of the moisture in the air blast. The Gayley process freezes out this moisture and furnishes dry air at a saving of 10 per cent of the coke. The gases from the top of the stack are worth saving. In composition they approximate producer gas and have a fuel value of 100 B. T. U. per cubic foot. There is a gain in using this gas at once because it leaves the stack at about 400°. This gas mixture is 24 per cent carbon monoxide, 16 per cent carbon dioxide, and 60 per cent nitrogen (from the air blast). It is led through a great pipe from the top of the stack to dust catchers and thence to the boilers, where it is burned to raise steam for the engines. It is more modern practice to explode this gas in gas engines. About one third the stack gas is burned directly in "stoves." These are steel towers filled with an open checkerwork of fire brick, which becomes highly heated. The gas is then turned off and cold air blown through to the base of the stack. As soon as this stove chills the air is led through another hot stove. Usually each stack is accompanied by four stoves. It is necessary to preheat the air blast in order to secure the highest possible temperature in the blast furnace.

Blast furnaces work continuously for many months until the lining wears away. They produce from 400 to 500 tons of pig iron per day. Some large furnaces use 1000 tons of 60 per cent ore, 500 tons of coke and approximately 250 tons of limestone daily. In addition five tons of air at 800° are required to produce one ton of pig iron.

Pig Iron. — The product of the blast furnace is termed *pig iron.* It is only about 92–94 per cent iron, the usual impurities being about 3 per cent carbon along with some sulfur, silicon, manganese and phosphorus. Much of this iron is cast into pigs for convenience in handling and then shipped to the various markets. It is remelted at the foundries (by coke in a cupola) and cast into such shapes as are needed for radiators, stoves, wheels, and a thousand useful articles. Pig iron is cast iron, but there are two types, depending on the rate of cooling. If poured into a metallic mold so that the liquid is chilled suddenly the carbon does not have time to separate as graphite, but remains uniformly distributed as cementite, Fe_3C. The product is white, very hard and very brittle. If cooled more slowly in sand molds, gray cast iron results. In this, part of the carbon has had time to separate as graphite. It is not nearly so hard as the white variety.

Such metal melts at about 1150°, while pure iron melts at about 1530°. Cast iron is hard, but low in tensile strength. It cannot be welded or forged, but it expands enough on cooling to completely fill the mold.

Wrought Iron. — To make a tough iron suitable for anchors, horseshoes, etc., it has long been the practice to purify melted pig iron on a bed of iron oxide in the puddling furnace. This is merely a small reverberatory furnace so built that heat is reflected and radiated down on the charge from the low roof of the furnace (Fig. 120). The pig iron melts, but as the impurities are burned out by the oxygen of the scale or ore on which it rests, its melting point rises and the metal becomes plastic rather than fluid. Limestone may be added as a flux. The metal is worked by the "puddler," using a long "rabble," and is finally removed in balls weighing about 100 pounds. Under the hammer or in the rolls the fluid slag is squeezed out, leaving nearly pure iron in fibers separated by thin films of slag. The product is extremely tough and strong, but not as hard as cast iron.

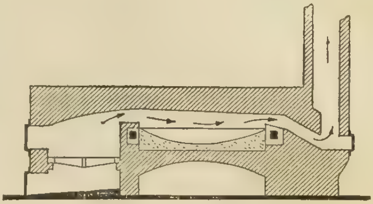


FIG. 120

In recent years wrought iron has been largely replaced by low carbon steel (0.2 per cent carbon or less), which is just as tough and is made more rapidly.

Steel. — Impurities are usually things to be gotten rid of, but in the case of iron this idea has to be modified. Pure iron is far surpassed in useful properties by iron containing from 0.2 to 2 per cent of carbon, a product known as steel. Of late years, we have even gone so far as to add manganese, chromium, nickel, vanadium, tungsten and other elements, so that some steels contain four or five elements. Pig iron contains enough carbon to make a hard steel, but the sulfur, silicon, etc., are injurious and must be removed. The only way to do this is to oxidize everything but the iron. Volatile oxides are blown out and the others unite with a flux to form a fusible slag easily separated by gravity. This is usually done in a Bessemer converter or in an open-hearth furnace.

The Bessemer Process. — Kelly, an American, proved, in 1852, that the impurities in melted pig iron could be burned out by a blast of air. It was three years later that Bessemer, the Englishman, discovered and patented the same process. This invention enormously increased the world's steel production and thus made possible the great era of railroad building that marked the latter half of the past century.

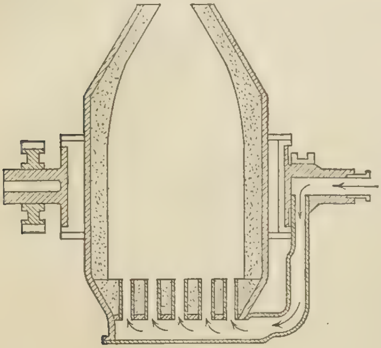


Fig. 121

The Bessemer converter (Fig. 121) is a huge steel egg lined with dolomite or siliceous rock, as desired. In a false bottom are many small holes. Below is the wind box into which air is forced through a hollow trunnion. The whole converter can be tilted to any angle. Molten iron is poured in while the converter is nearly horizontal, air turned on and the converter raised. Air bubbling up from the small holes oxidizes the carbon, silicon, sulfur, phosphorus and manganese with so much evolution of heat that the iron becomes even more fluid. A dazzling flame and showers of sparks present a magnificent spectacle. After 15–20 minutes the impurities are oxidized and the converter tilted to pour its contents into a ladle, from which it is poured into a series of ingot molds. At the moment of pouring, the desired amount of carbon, together with manganese or other elements, is added to the ladle. Since there is much air trapped in pouring, there is danger of weak places in steel rails where such bubbles are found. It is customary to add deoxidizers, which unite with oxygen and form a light slag floating to the top. Manganese has long been used for this purpose, but in the last decade aluminum shot has become popular with the steel maker, as has silicon or rather ferrosilicon.

At each "blow" 15 tons of steel are made, so the process is rapid, too rapid for the highest quality. Iron containing much phosphorus must be blown in a converter lined with dolomite or some other basic material. The phosphorus pentoxide formed reacts with this lining to form calcium and magnesium phosphates.

In the United States the converters are usually "acid-lined," that is, faced with siliceous rock, since the ores usually contain very little phosphorus.

The Open-hearth Process. — The open-hearth converter is a furnace with a wide, saucer-shaped hearth and a low roof (Fig. 122). A charge of pig iron and rusty scrap is added with limestone sufficient for fluxing off the impurities. The fuel is producer gas or an oil spray burning above the charge. The air and gas are both preheated by passing through a checkerwork of fire brick. The hot gaseous products of combustion pass off through another fire brick chamber. By frequently reversing the direction of the gases great economy of heating is secured. This is the Siemens regenerative process. About 50 tons of steel are produced every eight hours. The process somewhat resembles the puddling process in that the oxygen needed is derived from rusty iron or a bed of iron ore. The necessary carbon, manganese, etc., are added at the moment of pouring. In this country open-hearth furnaces are lined with magnesite.

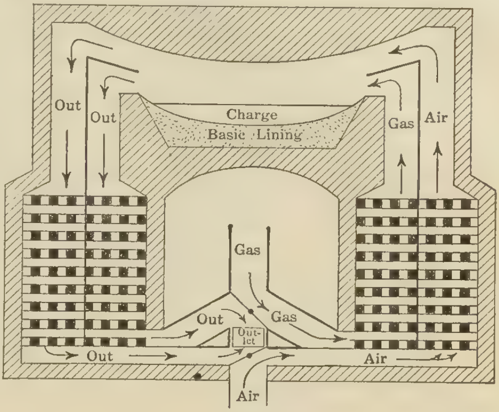


FIG. 122

EXERCISE 1. — What metal would be best for fire bars — wrought iron or high-carbon steel? What metal would be best for wire?

Since nearly one fourth of all iron and steel is lost by rust every year, it is essential that the blast furnaces keep up the incessant struggle with rust. After all, hematite ore is nothing but rust. Slosson says, "Without knowing the value of iron rust man could attain only to the culture of the Aztecs and Incas, the ancient Egyptians and Assyrians. The prosperity of modern states is dependent on the amount of iron rust which they possess and utilize. England, the United States, Germany, all nations are competing to see which one can dig the most iron rust out of the ground and make out of it railroads, bridges, buildings, machinery, battleships and such other tools and toys and then let them relapse into rust again. Civilization can be measured by the amount of iron rusted per capita or, better, the amount rescued from "rust."

Read Slosson's *Creative Chemistry* for his full story of iron, including a discussion of methods of rust-proofing.

Of the world's annual production of 72,000,000 tons of iron the United States makes about 30,000,000 tons. The Age of Steel had not fully arrived in 1868 when steel sold at $160 per ton. But by 1910 great improvements in manufacture and transportation reduced the cost to $28 per ton.

Alloy Steels. — Silicon, aluminum, manganese and titanium are added to steels at the moment of casting as "scavengers," to remove air bubbles. It is even proposed to use "mischmetal" for that purpose. Steel so cleansed is as much as 40 per cent stronger. But some of these elements, and a number of others, are also added to form valuable alloys with the steel. These alloy steels have brought about a series of revolutions in various industrial fields in which steel plays an important part.

Manganese Steel (12 to 14 per cent Mn) is very hard and tough. It is used in grinding machinery and burglar-proof safes.

Tungsten Steel (10 to 25 per cent W) is self-hardening; that is, a tool of this material hardens on cooling in air without being quenched in oil or water. It also holds its temper when the tool is worked until red-hot from friction. Before the invention of this steel the speed of lathe work was seriously retarded by loss of temper in the cutting tools. Now the use of tungsten steel has multiplied several times the output capacity of the machine shops of the world.

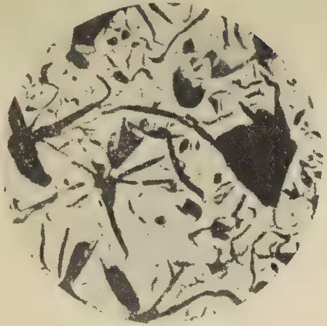
Exercise 2. — What influence has carborundum had on the speed of machine shop work?

Molybdenum Steel (6 to 7 per cent Mo). During the Great War, Germany suffered from a shortage of tungsten. They imported molybdenite from Norway and forced molybdenum to do the work of tungsten in high-speed tools. In addition such steels stand erosion well and were probably used in gun linings.

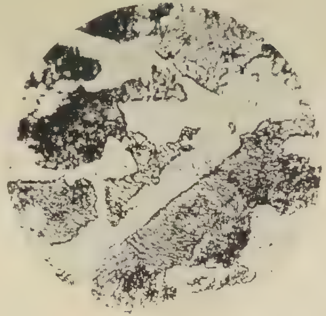
Vanadium Steel (0.1 to 0.4 per cent Va). When steel is desired to stand the heaviest shocks and vibrations, nothing is quite so effective as adding vanadium. Axles, cranks and piston-rods are made of this alloy.

"Chrome" Steel (2 to 4 per cent Cr). Chromium makes steel extremely hard. Cutting tools of special hardness and armor plate are made of this alloy.

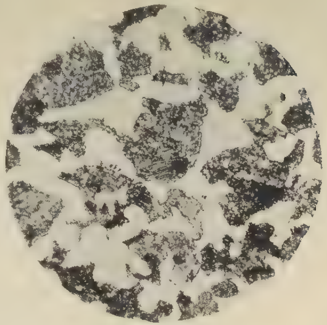
Pig Iron, 125 diameters

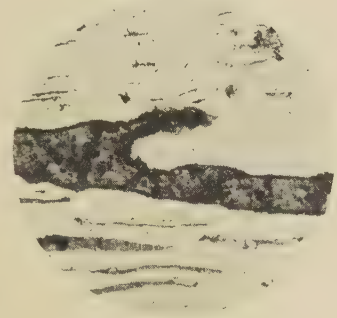


A Commercial Steel, slowly cooled from 850°, 500 diameters

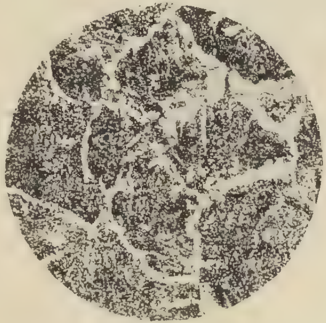


Auto Spring, hardened and tempered, 500 diameters

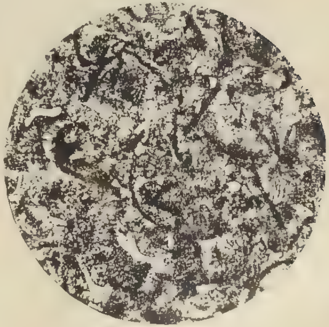




Wrought Iron, longitudinal section, 125 diameters



Same Commercial Steel, 0.5 per cent carbon, 125 diameters



Gray Cast Iron, 125 diameters

The above microphotographs of iron and steel were made by Professor James C. McCullough

"Duriron" (15 per cent Si). This hard but brittle alloy resists the attack of hot concentrated nitric and sulfuric acids and so has many uses in chemical manufacture. It is difficult to machine.

The Heat Treatment of Steels. — In steel above 900° the carbon is combined with part of the iron as cementite, Fe_3C. If cooled very suddenly this remains in a solid solution in the rest of the iron and gives the steel its characteristic hardness. But if cooled more slowly, at about 700° cementite crystals separate and appear in alternate layers or strata with the pure iron (ferrite). This mixture is called pearlite and has much of the softness and toughness of pure iron. A chilled tool can be reheated to any desired temperature and then cooled slowly enough to permit various crystalline arrangements to develop. This is tempering and by it any degree of hardness or toughness may be secured. The influence of such heat treatment on the structure of steels, and other alloys as well, is now studied by polishing the surface of the alloy, etching with chemicals that attack one compound more than another, and examining the etched surface with the microscope. This study is called metallography. Microphotographs of different steels show that their microstructure is far from homogeneous. An excellent discussion of the heat treatment of steels is found in the *Journal of the American Heat Treaters' Association*, Oct. 1918, by Burleigh.

Properties of Pure Iron. — The pure element has a density of 7.8 and is very ductile and malleable. It melts at about 1530°. It is not hardened by sudden cooling like steel. Chemically it is rather active, rapidly displacing hydrogen from acids. It rusts slowly in water (absence of air), displacing hydrogen. Weak acids, even carbonic, hasten this greatly. Consequently bases inhibit rusting. In moist air the metal rusts rapidly with formation of $2\ Fe_2O_3.3\ H_2O$ as a loose, soft scale. Iron is sometimes rustproofed by exposing the red-hot metal to steam. A coherent black scale, Fe_3O_4, is formed, and this protects the metal beneath. Chemically, it is the same as hammer scale of the rolling mill or blacksmith's anvil. It is always formed by oxidation of iron at high temperatures. Like manganese iron is rendered passive when dipped in strong oxidizing acids. Passive iron will not displace copper from solutions of copper salts. Unfortunately its passivity is easily destroyed by a scratch or a shock.

Ferrous Compounds

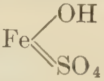
Ferrous Oxide, FeO, and Hydroxide, $Fe(OH)_2$. — The black oxide is prepared by heating the dry oxalate, FeC_2O_4. By passing hydrogen over the heated oxide it is easily reduced to the metal. The product, a fine powder, ignites in contact with the air, hence the name "pyrophoric iron." Ferrous hydroxide when precipitated in absence of air by solutions containing no dissolved oxygen is white. On exposure to air it is oxidized instantly to a green compound and in time to the red ferric hydroxide. In solubility it ranks with the hydroxides of bivalent manganese and magnesium and, like them, is dissolved by solutions of ammonium salts. (Why?) Since ferrous carbonate exists the hydroxide must be a strong base (unlike ferric hydroxide) and its common salts must suffer very little hydrolysis.

Ferrous Chloride, $FeCl_2$, is prepared by dissolving iron in hydrochloric acid. From this solution it crystallizes as $FeCl_2.4\,H_2O$, blue in absence of air, but green in presence of air. The anhydrous salt is made by passing dry hydrogen chloride over iron wire or filings. Since ferrous chloride is much more soluble than the sulfate, it is more convenient to set up hydrogen sulfide generators with hydrochloric than with sulfuric acid. Ferrous chloride is easily oxidized:

$$2\,FeCl_2 + Cl_2 \rightarrow 2\,FeCl_3.$$

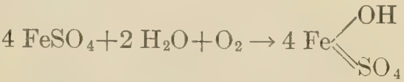
Ferrous Sulfate, $FeSO_4$.—Although ferrous sulfate can be made by the action of dilute sulfuric acid on iron, it is usually secured as a by-product of the pickling of iron and steel. Scale (oxide) is removed by immersion in dilute sulfuric acid. The ferrous sulfate formed is recovered from solution in large quantity. In some places heaps of moist iron pyrites are allowed to oxidize in the air and the ferrous sulfate formed leached out:

$$2\,FeS_2 + 7\,O_2 + 2\,H_2O \rightarrow 2\,FeSO_4 + 2\,H_2SO_4.$$

The crystallized salt, $FeSO_4.7\,H_2O$, is used in water purification because, when added to water with lime, the hydroxide formed drags down dirt and bacteria in settling. A small amount is used in making iron tannate inks.[1] These contain tannin, which with ferrous sulfate forms ferrous tannate, easily oxidized to black férric tannate. However, a trace of sulfuric acid prevents this in the bottle. When applied to the paper, this free acid is neutralized by basic material present and the oxygen of the air converts soluble ferrous tannate into black and insoluble ferric tannate. To give immediate color to the ink a dye is added. In the last few years there has been a large demand for ferrous sulfate in the dye industry. The double salt, $(NH_4)_2SO_4.FeSO_4.6H_2O$, is not an alum. (Why?) It is very stable, while the simple sulfate oxidizes readily in the air. Solutions of ferrous sulfate often contain a yellowish precipitate which is basic ferric sulfate,  $Fe\begin{array}{l}\diagup OH\\ \diagdown SO_4\end{array}$. A strip of iron and a little free acid prevent this oxidation.

---

[1] *Removal of Ink Spots and Other Stains.* The *Scientific American* Supplement of Aug. 4, 1917 (page 71) gives a full discussion of the subject.



$$4\,FeSO_4+2\,H_2O+O_2 \rightarrow 4\,Fe\begin{array}{l}\diagup OH\\ \diagdown SO_4\end{array}$$

Other Ferrous Salts. — ***Ferrous sulfide, FeS,*** is a black solid formed by heating together scrap iron and sulfur. It is possible to make it by heating iron pyrites in absence of air ($FeS_2 \rightarrow FeS + S$). As a laboratory source of hydrogen sulfide, it has a limited use. ***Ferrous carbonate, $FeCO_3$,*** occurs in England as the mineral siderite. It is soluble in waters containing carbon dioxide (the bicarbonate forms) and hence is precipitated in some "chalybeate" springs. In the air this bicarbonate is oxidized with formation of brown stains, objectionable in the laundry and in dye plants.

EXERCISE 3. — Write the oxidation equations for the action of dilute nitric acid on ferrous sulfate in the presence of sulfuric acid. When dilute nitric acid oxidizes anything, it breaks up as follows: $2HNO_3 \rightarrow H_2O + 2NO + (3O)$.

EXERCISE 4. — Write the equations representing the oxidation of ferrous chloride by potassium permanganate in a dilute hydrochloric acid solution.

FERRIC COMPOUNDS

Ferric Oxide, Fe_2O_3, and Hydroxide, $Fe(OH)_3$. — Hematite ore is Fe_2O_3, but a finer form, used as a pigment under the name Venetian red, is prepared by precipitation and ignition. Lime is added to a ferrous sulfate solution and the hydroxide allowed to oxidize in the air. Calcination of the product yields the oxide:

$$2\,Fe(OH)_3 \rightarrow Fe_2O_3+3\,H_2O.$$

Ferric Hydroxide. — This gelatinous precipitate is thrown down when any soluble base is added to a solution of a ferric salt. It dissolves in acids but not in alkalies (unlike the hydroxides of chromium and aluminum). On drying this red-brown hydroxide loses water so gradually that it is probable it is merely a more or less hydrated form of the oxide, $Fe_2O_3 \, x \, H_2O$. On adding a concentrated solution of ferric chloride to boiling water, a rich red colloidal suspension of the hydroxide is formed. Hydrolysis is marked at 100°. (See chapter on Colloids.)

$$FeCl_3 + 3\,H_2O \leftrightarrows Fe(OH)_3 + 3\,HCl$$

"Dialyzed iron" is a preparation of colloidal ferric hydroxide used sometimes as an antidote for arsenic poisoning.

Ferric Chloride, $FeCl_3$. — The preparation of ferric chloride consists in passing chlorine into a solution of ferrous chloride. It is a yellow, deliquescent and very soluble solid. It is hydrolyzed to such an extent that on heating it to dryness nothing but the oxide, Fe_2O_3, remains. The anhydrous form must be prepared by passing chlorine over hot iron (Fig. 123). The salt sublimes on heating, so it is possible to measure its molecular weight at different temperatures. (How?) At 750° the formula must be $FeCl_3$, but at 450° the formula must be Fe_2Cl_6.

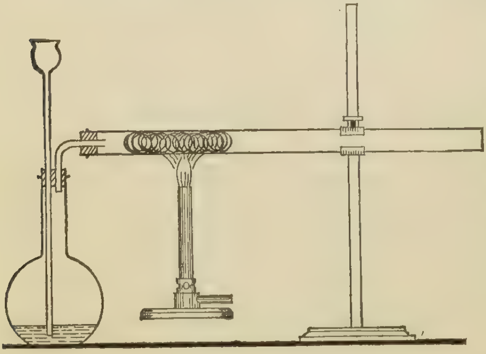


Fig. 123

Other Ferric Salts.— *Ferric sulfate*, $Fe_2(SO_4)_3$, is readily formed by oxidizing ferrous sulfate in a sulfuric acid solution. It unites with the alkali sulfates to form alums. The black *ferric sulfide*, Fe_2S_3, is precipitated when ammonium sulfide is added to solutions of ferric salts. *Ferric thiocyanate*, $Fe(CNS)_3$, is a red, soluble compound produced whenever potassium thiocyanate is added to a solution of a ferric salt. Its formation is a delicate test for iron in the ferric condition.

Exercise 5. — Represent by equations the reductive of ferric chloride by stannous chloride or by hydrogen sulfide.

The Complex Cyanides. — Addition of potassium cyanide to a solution of a ferrous salt produces a precipitate of ferrous cyanide, readily soluble in an excess of the reagent:

$$\mathrm{FeSO_4 + 2\ KCN \rightarrow Fe(CN)_2,}$$
$$\mathrm{Fe(CN)_2 + 4\ KCN \rightarrow K_4Fe(CN)_6.}$$

The complex salt, potassium ferrocyanide, $K_4Fe(CN)_6$, ionizes as follows:

$$\mathrm{K_4Fe(CN)_6 \leftrightarrows 4\ \overset{+}{K} + \overset{----}{Fe(CN)_6}.}$$

The ferrocyanide ion is very stable, yielding no simple iron ions. With ferric salts a precipitate called Prussian blue is formed. It is really ferric ferrocyanide:

$$\mathrm{4\ FeCl_3 + 3\ K_4Fe(CN)_6 \rightarrow Fe_4[Fe(CN)_6]_3 + 12\ KCl.}$$

When chlorine is passed into a solution of the yellow potassium ferrocyanide the reddish potassium ferricyanide is formed:

$$\mathrm{Cl_2 + 2\ K_4Fe(CN)_6 \rightarrow 2\ KCl + 2\ K_3Fe(CN)_6.}$$

This salt reacts with ferrous salts to form insoluble Turnbull's blue, which is ferrous ferricyanide:

$$\mathrm{3\ FeSO_4 + 2\ K_3Fe(CN)_6 \rightarrow Fe_3[Fe(CN)_6]_2.}$$

Blue Prints. — Certain ferric salts in the presence of light are reduced to ferrous salts, so a paper soaked in ferric ammonium citrate and potassium ferricyanide and dried (all in a dark room) is subject to change on exposure to light. A design or drawing laid over this blue print paper allows light to reduce the ferric ammonium citrate to the ferrous salt wherever the paper is unprotected. On dropping the exposed paper into water the two salts dissolve and react to form Turnbull's blue. Where heavy lines in the drawing protected the paper there is no reduction by light and the salts are washed out, leaving white lines on a blue background.

Tests. — Ferrous salts are recognized by reaction with potassium ferricyanide to form Turnbull's blue. Ferric salts react with any alkali thiocyanate to form soluble, red ferric thiocyanate. They also react with potassium ferrocyanide to form insoluble Prussian blue. Ferric hydroxide is red, insoluble, and differs from the hydroxides of chromium and aluminum in not dissolving in sodium hydroxide.

Cobalt

Occurrence and Preparation. — Cobalt was first prepared by Brandt in 1735, but has never become an important element. It occurs in smaltite, $CoAs_2$, and cobaltite, $CoAsS$, as well as in a combination with nickel and arsenic. Some cobalt ores are found in Canada and New Caledonia, but they are not very abundant. It is best prepared by the Goldschmidt process.

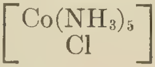
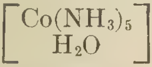
Properties. — The metal is hard and white like iron, yet it is also malleable and ductile. It melts at 1478° and has a density of 8.5. It displaces hydrogen slowly from ordinary dilute acids, but is readily attacked by nitric acid. It forms remarkable acid-resisting alloys with some other metals. Cobalt may be used in electroplating as a substitute for nickel, but that will be mainly a matter of relative cost.

Oxides and Hydroxides. — Cobalt forms two series of compounds, like iron, with valences of 2 and 3. Cobaltous oxide, CoO, and cobaltic oxide, Co_2O_3, are the starting points for two series of salts. The oxide Co_3O_4 is really a sort of a salt like Fe_3O_4. The black cobaltous oxide is used in giving a blue color to glass, enamels and other silicates. Cobaltous hydroxide, $Co(OH)_2$, is precipitated as a blue basic salt rather than as a simple hydroxide, but on boiling it turns into the pink hydroxide. Heated dry in absence of air it yields cobaltous oxide.

Exercise 6. — Cobaltous hydroxide is about as insoluble as magnesium hydroxide. Would it dissolve in ammonium salts?

Cobalt Salts. — Cobaltic salts are not stable (except the amines), but many cobaltous salts exist. They are all pink in solution, but when dry many of them turn blue. A *sympathetic ink* was made on that principle. The writing in the pale pink cobalt salt solution ($CoCl_2$, usually) was invisible, but on drying cautiously over a flame the blue color of the anhydrous salt became conspicuous.

Cobalt Sulfide, CoS, dissolves in dilute hydrochloric acid with extreme slowness (like nickel sulfide) and hence these two may be separated from the sulfides of iron, zinc and manganese. The difference in solubility is mainly one of speed. *Cobalt nitrate*, $Co(NO_3)_2$, is used in blowpipe analysis. Aluminum hydroxide moistened with a drop of a solution of this salt turns blue under the blowpipe flame. (Test for Al.) A similar reaction with zinc hydroxide yields a green compound. Cobalt silicate as found in glass, porcelain, beads, and enamel is blue. A pigment called smalt is made by fusing cobaltous oxide with sand and grinding the blue silicate to a powder.

The Cobalt Amines. — Ammonia reacts with cobalt compounds in solution to form a great variety of peculiar products called the cobalt amines. The oxygen of the air raises them out of the cobaltous class into the cobaltic. Among such compounds are hexamine cobaltic chloride, $Co(NH_3)_6Cl_3$, chloropentamine cobaltic chloride,  $\begin{bmatrix} Co(NH_3)_5 \\ Cl \end{bmatrix} Cl_2$, and aquopentamine cobaltic chloride,  $\begin{bmatrix} Co(NH_3)_5 \\ H_2O \end{bmatrix} Cl_3$. Werner made a great number of such ammonia compounds and developed an interesting theory of the inner linkage of atoms and groups. (Review chromium salts in this connection.)

NICKEL

Occurrence and Preparation. — Nickel occurs associated with arsenic or sulfur, or both, as in nicollite, NiAs, and nickel glance, NiAsS. The Ontario pentlandite is a sulfide of nickel, copper and arsenic. Most ores carry some cobalt. The New Caledonia ore is a silicate of nickel and magnesium. The Ontario ores are roasted and run through a Bessemer process. The "matte," or melted mixture of sulfides of nickel, copper and iron, is "blown" until the iron is removed in the slag, leaving the sulfides of nickel and copper. There are two or three methods of separating the nickel from the copper. By the Hybinette process the matte is roasted to remove the bulk of the sulfur and leached with 10 per cent sulfuric acid, which dissolves out most of the copper but very little of the nickel. The residue is melted and cast into anodes for purification by electrolysis. An alloy of copper and nickel obtained from the Ontario ores is used as "monel metal," a tough, ductile alloy which resists corrosion. It can be cast and machines well.

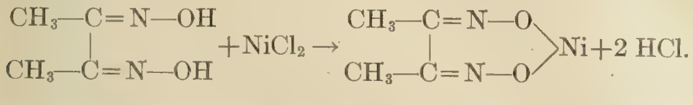
Properties. — Nickel is a white, magnetic metal resembling iron. It melts at 1452° and has a density of 8.8. It is hard, malleable, takes a high polish and does not tarnish readily in the air. Hence many common metallic objects are nickel plated. Iron is first copper plated. Nickel has some use in alloys such as monel metal, nickel steel, German silver and nickel coins. Despite the white color our common 5-cent piece is 75 per cent copper and only 25 per cent nickel. Finely divided nickel is used as the catalyst in hydrogenating liquid fats to make solid fats.

Nickel Compounds. — There are two series of nickel salts derived from nickelous oxide, NiO, and nickelic oxide, Ni_2O_3. Nickelous-nickelic oxide, Ni_3O_4, is a sort of salt resembling Fe_3O_4 and Co_3O_4. All nickel salts are green when hydrated. Nickel sulfide, NiS, is precipitated as a black powder when ammonium sulfide is added to a solution of a nickel salt. Excess of the reagent peptizes it into a colloidal suspension that runs through the filter paper. Green nickelous hydroxide, $Ni(OH)_2$, is precipitated by addition of a base to a solution of a nickel salt, but if a hypochlorite be added to a nickel salt solution the black nickelic hydroxide, $Ni(OH)_3$, is thrown down. Much nickel sulfate, $NiSO_4.7\ H_2O$, is separated from the bath in electrolytic copper refining. The double salt, $(NH_4)_2SO_4.NiSO_4.6\ H_2O$, is commonly used as the bath in nickel plating. The chloride, $NiCl_2.6\ H_2O$, and the nitrate, $Ni(NO_3)_2.6\ H_2O$ are readily prepared.

Nickel Carbonyl, $Ni(CO)_4$.— This volatile liquid is formed when carbon monoxide is passed over nickel below 80°. The liquid boils at 43° and its vapor explodes at 60°. However, when diluted with carbon monoxide it decomposes gradually into nickel and carbon monoxide. By the Mond process (used in England) nickel ores are worked up to yield a finely divided metallic powder of nickel, copper and iron. Carbon monoxide is passed over this powder at 50° to 80°, forming nickel carbonyl. This latter gas is then decomposed by passing it through a tower containing shot nickel heated to about 200°. Layers of nickel deposit on the shot, while the carbon monoxide liberated is returned to the carbonyl towers.

The Edison Storage Cell uses nickelic hydroxide and iron dust as the poles and a 21 per cent solution of potassium hydroxide as the electrolyte. On discharge the trivalent nickel is reduced to the bivalent form, while bivalent iron is oxidized to the trivalent form. The action is reversed on charge. The voltage of this cell is lower than that of the common lead storage cell, but Edison's cell is lighter and more durable.

Tests for Nickel and Cobalt.—Nickel salts react with dimethylgyoxime to give a scarlet precipitate.



Cobalt compounds give a blue bead with borax or microcosmic salt, while nickel compounds yield a brown bead in the oxidizing flame. Cobalt salts react with nitroso-β-naphthol to yield a brick-red precipitate and in the presence of ammonia, with phenylthiohydantoic acid to yield a red-brown precipitate.

CHAPTER XXXVIII

THE PLATINUM METALS

	Atomic Weight	Density	Melting Point	Oxides
Ruthenium	101.7	12.3	1900°	RuO, Ru_2O_3, RuO_2, RuO_4
Rhodium	102.9	12.44	1907°	RhO, Rh_2O_3, RhO_2
Palladium	106.7	11.4	1549°	PdO, PdO_2
Osmium	190.9	22.5	2200°	OsO, Os_2O_3, OsO_2, OsO_4
Iridium	193.1	22.41	2300°	Ir_2O_3, IrO_2
Platinum	195.2	21.5	1755°	PtO, PtO_2

In the final column of the periodic table are three groups of three elements each. One of these groups, iron, cobalt and nickel has been studied already. The platinum metals are rare and are found usually as the free elements. They occur in alluvial sands in the Ural mountains of Russia, in Colombia, the Pacific coast states, Brazil and Borneo. Platinum forms the greater part of the extracted grains or nuggets. Russia leads in production.

Platinum. — It is unfortunate that this element is so rare, for it is most useful. Its high melting point, 1755°, its resistance to chemical corrosion and its remarkable powers as a catalyst make it almost indispensable. In the laboratory it is used in the form of crucibles, wire and sheet. Certain precautions must be taken in its use, as it is attacked by chlorine and aqua regia as well as by fused alkalies. It also alloys with a number of easily reducible metals. When hot it is permeable to hydrogen, so easily reduced compounds of certain metals should not be heated in platinum dishes over a gas flame. The coefficient of expansion of this metal is so near that of soft glass that it is used for leading-in wires in laboratory apparatus and in electric light bulbs. However, a cheaper alloy has been found for that purpose. Contact points for spark ignition were formerly made of platinum but now are made of the cheaper tungsten. It is easy to weld platinum at a red heat and in general it may be classed as rather malleable and ductile. It also conducts electricity moderately well.

When ammonium chlorplatinate, $(NH_4)_2PtCl_6$, is ignited a finely divided form of the metal called *platinum sponge* is secured. Heating asbestos soaked in chlorplatinic acid yields the metal in fine particles scattered through the asbestos. Such forms of platinum are used as catalysts in various industries, notably in the contact process of making sulfuric acid. The Ostwald process for oxidizing ammonia to nitric acid uses platinum gauze covered with reduced platinum in a spongy form. Oxygen is condensed on the surface of platinum, while hydrogen is actually dissolved in it. This explains why a platinum wire with spongy surface ignites an explosive mixture of oxygen and hydrogen. The gases are brought in closer contact with each other by the platinum. The vapor of methyl alcohol is ignited in the air by a fine platinum wire. Cigar lighters and gas lighters have been made on this principle.

During the Great War the unsettled condition of Russia cut off this chief source of the metal and as a result highly necessary munition manufactures were seriously handicapped. The price, always higher than that of gold (in recent years), soared to extravagant heights. Women were urged not to use it in jewelry as heretofore, so that chemical industries might not be crippled. Women who use platinum jewelry at any time are taking from scientific use a metal for which there is no adequate substitute and of which there is never enough for scientific needs. Some platinum is found alloyed with gold in the Pacific states, but the amount separated is small. The tips of fountain pens are made of a very hard platinum-iridium-osmium alloy.

Compounds of Platinum. — Platinum forms two series of compounds with valence of 2 and 4. *Platinum chloride*, $PtCl_2$, is formed when chlorine is passed over the finely divided metal at 240°–250°. With hydrochloric acid it forms chloroplatinous acid, H_2PtCl_4. The potassium salt, K_2PtCl_4, is used in photography. Black platinous hydroxide, $Pt(OH)_2$, is formed by addition of a base to a solution of platinous chloride. On gently heating it yields the oxide and at higher temperatures the metal itself. Barium platinocyanide, $BaPt(CN)_4.4\,H_2O$, fluoresces when bombarded by X-rays and hence is used for X-ray screens.

Platinum dissolves in aqua regia with formation of the soluble *chloroplatinic acid*, H_2PtCl_6. This is the reagent used in the quantitative determination of potassium, as the potassium salt, K_2PtCl_6, is insoluble. That the acid ionizes as follows ($H_2PtCl_6 \leftrightarrows 2\,\overset{+}{H} + \overset{--}{PtCl_6}$) is proved by addition of silver nitrate. No silver chloride is precipitated, only silver chloroplatinate, Ag_2PtCl_6.

Platinic chloride, $PtCl_4$, is formed by heating chloroplatinic acid in a current of chlorine at 360°. It reacts with water to give the soluble $H_2PtCl_4O.4\,H_2O$. With bases, chloroplatinic acid yields a precipitate of *platinic hydroxide* $Pt(OH_4)$ which reacts with excess base to form platinates. The sulfides, PtS and PtS_2, are precipitated in the expected way with hydrogen sulfide. They dissolve in alkali polysulfides, as does arsenic. The complex amines of platinum are numerous.

Palladium. — Palladium is associated with platinum in the natural alloys and resembles it in appearance and some properties. Yet it is more like silver in that nitric acid dissolves it. Then, too, it is softer, lighter and melts more easily than platinum. In valence it resembles the other platinum metals. Its most interesting property is the ability of finely divided palladium to absorb 800 volumes of hydrogen — 900 volumes if a strip of the metal be made the cathode of an electrolytic cell. It is remarkable that such adsorbed hydrogen displaces from solutions of their salts metals below it in the electromotive series, although a stream of hydrogen gas does not do so. Probably because of this activity of hydrogen so adsorbed palladium sponge is used with hydrogen in organic reduction reactions. Palladium possesses such great resistance to the attack of oxygen, moisture and hydrogen sulfide that it is sometimes used for the inner mechanism of watches, fine balance beams, surgical instruments and special apparatus. It is used in soldering platinum and as a catalyst.

Palladium dichloride, $PdCl_2.2\,H_2O$, is made by dissolving the spongy metal in hydrochloric acid, a method that obviously must fail with platinum. The tetrachloride, $PdCl_4$, is not very stable. The salt, K_2PdCl_6, and the complex amines are suggestive of certain platinum compounds.

Rhodium. — Rhodium is not attacked by aqua regia or any acid, but reacts with chlorine. There are two chlorides, $RhCl_2$

and $RhCl_3$. Three oxides are known; RhO, Rh_2O_3, and RhO_2. The complex amines resemble those of cobalt. Rhodium is harder than platinum.

Iridium. — This element resembles rhodium in its resistance to aqua regia. Since it is very hard and not oxidized at high temperatures it is useful for some apparatus and in the preparation of alloy tips for fountain pens. When native platinum is warmed with aqua regia, only the platinum dissolves, leaving iridium and osmium. Iridium forms three chlorides: $IrCl_2$, $IrCl_3$ and $IrCl_4$. Such complex chlorides as $K_3IrCl_6.6\ H_2O$ and K_2IrCl_6 are better known.

Osmium. — Osmium is remarkable in having the greatest density of any substance known. It is gray like iron, but, unlike that metal, resists the attack of aqua regia. However, it unites easily with oxygen when heated, forming the tetroxide, OsO_4. This oxide is a white solid, slowly soluble in water. Its vapor is most unpleasant in odor and is extremely poisonous. It is called "*osmic acid*" but in reality is not an acid nor even an acid anhydride. The substance is used to stain tissues, which it does by its powerful oxidizing properties. Animal tissue reduces it to the black finely divided metal. At the same time the tissues are hardened. There are four oxides: OsO, Os_2O_3, OsO_2 and OsO_4. The chlorides are $OsCl_2$, $OsCl_3$, and $OsCl_4$. Such salts as $K_3OsCl_6.6\ H_2O$ exist.

Ruthenium. — Ruthenium resembles osmium, especially in the formation of the volatile tetroxide, RuO_4, made by fusing the metal with potassium hydroxide and potassium nitrate. The dioxide RuO_2 is formed by heating ruthenium in a current of oxygen and Ru_2O_3 by heating in air. Chlorides and double salts are similar to those of osmium.

APPENDIX

Conversion Table

Metric and English Systems

1000 millimeters (mm.) = 1 meter
100 centimeters (cm.) = 1 meter
10 millimeters = 1 cm.

1000 grams = 1 Kilogram (Kg.)
1000 cubic centimeters = 1 liter

2.54 cm. = 1 inch
1 meter = 39.37 inches
1 liter = 1.06 quarts
1 gram = 15.4 grains
1 Kilo = 2.20 pounds
28.35 grams = 1 ounce

Pressure (or Tension) of Water Vapor in Millimeters of Mercury

Temperatre	Pressure	Temperature	Pressure
0°	4.6	21°	18.6
5°	6.5	22°	19.8
10°	9.2	23°	21.0
12°	10.5	24°	22.3
15°	12.7	25°	23.6
16°	13.6	26°	25.1
17°	14.4	27°	26.5
18°	15.4	28°	28.1
19°	16.4	29°	29.8
20°	17.5	30°	31.5

Weight in Grams of 1 Liter of Various Gases

(Standard conditions)

Air	1.2928	Hydrogen Chloride	1.6398
Ammonia	0.7708	Hydrogen Sulfide	1.5392
Argon	1.7809	Methane	0.7168
Carbon Dioxide	1.9768	Nitric Oxide	1.3402
Carbon Monoxide	1.2504	Nitrogen	1.2507
Chlorine	3.1674	Nitrous Oxide	1.9777
Helium	0.1782	Oxygen	1.4290
Hydrogen	0.0898	Sulfur Dioxide	2.9266

THE PERIODIC TABLE

O = 16

	PERIODS	GROUP O R —	GROUP I R_2O —	GROUP II RO —	GROUP III R_2O_3 —	GROUP IV RO_2 RH_4	GROUP V R_2O_5 RH_3	GROUP VI RO_3 RH_2	GROUP VII R_2O_7 RH	GROUP VIII RO_4 —		
Short Periods	1	He = 4	A B Li = 6.94	A B Be = 9.1	A B B = 10.9	A B C = 12	A B N = 14.01	A B O = 16	A B F = 19			
	2	Ne = 20.02	Na = 23	Mg = 24.32	Al = 27.1	Si = 28.3	P = 31.04	S = 32.06	Cl = 35.46			
Long Periods	3	A = 39.88	K = 39.10 Cu = 63.57	Ca = 40.07 Zn = 65.37	Sc = 44.1 Ga = 69.9	Ti = 48.1 Ge = 72.5	V = 51 As = 74.96	Cr = 52 Se = 79.2	Mn = 54.93 Br = 79.92	Fe = 55.84	Co = 58.97	Ni = 58.68
	4	Kr = 82.92	Rb = 85.45 Ag = 107.88	Sr = 87.63 Cd = 112.4	Y = 88.7 In = 114.8	Zr = 90.6 Sn = 118.7	Cb = 93.1 Sb = 120.2	Mo = 96 Te = 127.5	— I = 126.82	Ru = 101.7	Rh = 102.9	Pd = 106.7
	5	X = 130.2	Cs = 132.81	Ba = 137.37	La = 139	Ce = 140.25	Rare	Earth	Metals			
	6	—	Au = 197.2	Hg = 200.6	Tl = 204.0	Pb = 207.2	Ta = 181.5 Bi = 208	W = 184. —	— —	Os = 190.9	Ir = 193.1	Pt = 195.2
	7	Nt = 222	—	Ra = 226	—	Th = 232.4	—	U = 238.2	—			

INDEX

(The chief reference to a subject is in black face type. Proper names are set in small capitals.)

Absolute zero, 35, 40
Acetic acid, 320
Acetone, 319
Acetylene, 298
    series, 295
Acheson, 279
Acidimetry, 157
Acids, 137
Actinium, 509
Activity series of metals, 56
Adhesive tape, 447
Adsorption, 283, 354
Air a mixture, 205
Alcohols, 316
Aldehydes, 315, 316, **319**
Alkali metals, 370
Alkaline earth metals, 396
Allotropy, 163
Alloys, 273
Alloy steels, 534
Alpha rays, 504
Aluminates, 472
Aluminothermy, 364, 470
Aluminum, 466
    chloride, 473
    hydroxide, 471
    occurrence, 466
    oxide, 471
    preparation, 467
    properties, 469
    sulfate, 473
    uses, 469
Alums, 474
Alunite, 386, 474
Amalgamation process, 433
Ammonia, 221
    chemical properties, 226
    physical properties, 226
    preparation, 222, 223
    uses, 228
Ammonium, 391
    amalgam, 391
    bicarbonate, 230
    carbonate, 392
    chloride, 230, 391
    hydroxide, 229, 391
    nitrate, 392
    nitrite, 219, 392
    sulfate, 223, 229
    sulfide, 393
    tests for, 393
Ammono bases, 457
Ampere, 464
Amphoteric hydroxides, 448, 472
Anhydrides, 128
Aniline, 303
Anode, 140
Antichlor, 187
Antimony, 269
    nitrate, 271
    occurrence, 270
    oxides, 270
    preparation, 270
    properties, 270
    sulfate, 271
    sulfides, 272
    trichloride, 271
Apate, 251
Aquadag, 279
Aqua regia, 244
Argon, 213
Argon family, 213
Arrhenius, 142
Arsenic, 264
    acids, 267
    halides, 266
    occurrence, 264
    oxides, 266
    preparation, 264
    properties, 265
    sulfides, 268
Arsenious acid, 255
Arsine, 266
Artificial gems, 471
Artificial silk, 247, 325
Asphalt, 302
Atmosphere, 205
Atomic numbers, 201, 202
Atomic volumes, 196, 197
Atomic weights, 8, 83
    theory, 9
Atoms, 9
Auric chloride, 439
Avogadro's law, 41, 78, 82

Babbitt metal, 274, 275
Baking powders, 380
Balanced rations, 332
Balard, 117
Bancroft, 346
Barite, 409
Barium, 409
    chloride, 411
    hydroxide, 411
    nitrate, 411
    occurrence, 409
    oxides, 410
    sulfate, 409
    tests for, 411
Barometer, 37
Bases, 137
Bauxite, 467
Becquerel, 503
Benzene, 302
Benzene series, 295
Benzine, 301

Berkeley, 100
Beryllium, 458
Bessemer process, 532
Beta rays, 505
Bicarbonates, 287
Birkeland-Eyde process, 239
Bismuth, 272
    compounds, 273
    occurrence, 272
    preparation, 272
    properties, 273
    subnitrate, 273
Blanc fixe, 409
Blast furnace, 526
Bleaching powder, **129**, 400
Blue prints, 539
Boiler compounds, 407
Boiling point, 42
    rise, 96
Borax, 342, **344**
Bordeaux mixture, 431
Boric acid, 343
Boron, 342
Boyle's law, 33
Bragg, 202
Brass, 275
Brin's process, 15, 55
Bromic acid, 135
Bromine, 118
Bronze, 275
B. T. U., 22
Bucher process, 226, **382**
Burton process, 301
Butter, 322

Cadmium, 451
    hydroxide, **451**
    oxide, 451
    salts, 451
    tests for, 452
Cæsium, 394
Calcium, 396
    bisulfite, 179
    carbide, 225, 292, **404**
    carbonate, 397
    chloride, 402
    fluoride, 402
    hydroxide, 400
    oxide, 398
    phosphate, 403
    sulfate, 401
Calomel, 454
Calorie, 21
Cannizzaro, 83, 192
Carbides, 284
Carbohydrates, **324**, 330
Carbolic acid, 303
Carbon, 277, 283, 284
    cycle, 290
    dioxide, 284
        chemical properties, 286
        physical properties, 286
        preparation, 285
        snow, 286
        uses, 288
    disulfide, 291
    monoxide, 289
    tetrachloride, 291
Carbona, 291
Carbonates, 287
Carbonic acid, 287
Carborundum, 292
Carnallite, 583
Carnotite, 502
Castner's process, 374, **467**
Catalyst, 16, 27
Cathode, 140
Cavendish, 44, 236
Celestite, 411
Cell, dry, 523
    Daniell, 461
    electric, 460
    gravity, 461
    Nelson, 375
Celluloid, 247
Cellulose, **324**
Chalk, 397
Chance process, 378
Chapin, W. H., 38, 260
Charcoal, 281
    cocoanut, 283
Charles' law, 35
Chemical reactions, types of, 110
Chili saltpeter, 217, 231
Chloramic acid, 439
Chlorates, 133
Chlorauric acid, 439
Chloric acid, 132
Chlorine, **103**
    action on water, 110
    action on compounds, 109
    by electrolysis, 107
    chemical properties, 108
    commercial preparation, 106
    laboratory preparation, 103
    oxides of, 135
    physical properties, 107
    tests for, 112
    uses, 111
Chloroform, 314
Chlorophyl, 290
Chloroplatinic acid, 546
Chromates, 513, 517
Chrome alum, 516
Chromic anhydride, 572
    chloride, 515
    compounds, 515
    hydroxide, 516
Chromite, 517
Chromium, 510
    in steel, 534
    salts, 511
    tests for, 517
Chromous compounds, 515
Cleansing action of soap, 355
Coal, 280
    gas, 306, 307
    tar, 304
Cobalt, 540
    amines, 541
    hydroxides, 540
    nitrate, 540
    oxides, 540
    salts, 540
    tests for, 543
Coke, 280
    ovens, 223

- Colloidal ferric hydroxide, 352
  - gels, 357
  - gold, 351
  - silver, 351
  - soaps, 358
- Colloids, 346
  - applications of, 358
  - Brownian movement of, 347
  - coagulation of, 356
  - electric charge on, 348
  - irreversible, 354
  - preparation of, 349
  - protective, 356
  - reversible, 354
- Columbium, 498
- Combining weights, 5
- Combustion, 19
  - spontaneous, 23
- Common ion effect, 420
- Complex ammonia compounds, 230
  - salts, 368
- Concentration, 87
- Conductivity, 147
- Contact process, 184
- Copper, 424
  - ammonia compounds of, 431
  - carbonate, 431
  - complex cyanides of, 432
  - ferrocyanide, 431
  - metallurgy, 425
  - nitrate, 431
  - occurrence, 424
  - oxides, 429
  - properties, 427
  - tests for, 433
  - uses, 427
- Cordite, 246
- Corn syrup, 328
- Corrosive sublimate, 455
- Coulomb, 143, 463
- Cracking of oils, 301
- Crayons, 402
- Cream of tartar, 321
- Creosote, 305
- Crisco, 56
- Critical pressure, 17
  - temperature, 17, 43
- Crystal systems, 164
- Cupric hydroxide, 430
  - oxide, 429
  - sulfate, 430
  - sulfide, 430
- Cuprous bromide, 429
  - chloride, 428
  - iodide, 429
  - oxide, 428
- Curie, Madame, 504
  - Pierre, 504
- Cyanamide chart, 404
  - process, 225
- Cyanates, 293
- Cyanides, 293
- Cyanogen, 293
- Cycle of carbon in nature, 290

- Dalton's law, 92
- Davy, 117, 236, 312, 371 386
- Deacon's process, 106
- Deliquescence, 69
- Density, 66
- Determination of formula from analysis, 12
- Deville, 467
- Dewar flask, 212
- Dextrin, 326
- Dextrose, 327
- Dialysis, 353
- Diamond, 277
- Diastase, 329
- Dichromates, 513, 517
- Digestion, 331
- Dimethylglyotine, 543
- Disodium phosphate, 257
- Dobereiner's triads, 193
- Double salts, 368
- Dumas bulb, 81
- Duralumin, 275
- Duriron, 337
- Dust, 207
  - explosions, 24
- Dyeing, 475
- Dynamite, 245

- Edison storage cell, 542
- Efflorescence, 69
- Electric cells, 460
  - energy, 463
  - furnace, 498
- Electrochemistry, 459
- Electrolysis, 46, 140
- Electrolytic refining, 426
- Electromotive force, 461
  - series, 159, 460, 462
- Electrons, 144
- Electroplating, 428
- Elements, definition of, 2
- Emulsions, 352
- Emulsoids, 354
- Endothermic reactions, 21
- Energy, 1
- Enzymes, 328
- Epsom salts, 444
- Equations, 11
- Equilibrium, 413
  - constant, **418**
- Esters, **321**
- Ethereal salts, 321
- Ethers, 318
- Ethyl alcohol, 314, **317**
- Ethyl group, 314
- Ethylene, 297
  - bromide, 297
  - series, 295
- Exothermic reactions, 21
- Explosives, 245

- Faraday, 108, 140
- Faraday's law, 143
- Fats, 322, 330
- Fehling's solution, 428
- Ferric compounds, 537
  - chloride, 538
  - hydroxide, 538
  - oxide, 537
  - sulfate, 538
- Ferro-alloys, 364
- Ferrochrome, 510
- Ferrous carbonate, 537
  - chloride, 536

Ferrous compounds, 536
    hydroxide, 536
    oxide, 536
    sulfate, 536
    sulfide, 537
Ferrovanadium, 497
Flame, 310
Flame colors, 313
Flotation, 426
Fluorine, 118
Food, 330
    chart, 333
    fuel value of, 332
Formic acid, 320
Franklin, E. C., 226, 457
Frasch process, 161, 162
Frazer, 100
Freezing point lowering, 95, 139

Gamma rays, 506
Gas carbon, 280
    mantles, 496
    masks, 283
Gases, fuel value of, 310
    properties of, 33
Gasoline, 297, 304
Gay-Lussac's law, 52, 82, 117
Gels, 357
German silver, 275
Germanium, 496
Glass, 341
Glauber's salt, 380
Glucinum, 458
Glucose, **328**
Glycerine, 318
Gold, 438
    compounds, 439
    metallurgy, 438
    occurrence, 438
Goldschmidt's process, 364, 470
Graham's law of diffusion, 37
Gram molecular volume, 80
Graphite, 278
Gravity cell, 461
Greensands of New Jersey, 386
Guncotton, 246
Gunpowder, 245
Gypsum, 401

Haber process, 223
Hall, 467
Halogen acids, 124, 125
Halogens, **117**
    preparation, 118, 119
    properties, 120
    uses, 121
Hardness of water, 405
Hare, 292, 387
Harkins, 200
Heat of combustion, 21
    fusion, 42, 66
    vaporization, 43
Heat treatment of steel, 535
Helium, 214
Henry's law, 91
Heroult, 467
Holland, 100
Humidity, 208
Hydrates, 68
Hydrazine, 231
Hydrazoic acid, 231
Hydrocarbons, 295
Hydrocarbon derivatives, **314**
Hydrofluoric acid, 125
Hydrogen, **44**
    bromide, 122, 124, 125
    chemical properties, 50
    fluoride, 122, 124, 125
    iodide, 122, 124, 125
    physical properties, 49
    preparation, 44
    purification, 49
    uses, 56
Hydrogen, chemical properties, 115
    chloride, 112
    physical properties, 114
    preparation, 112
    tests for, 116
    uses, 116
Hydrogen peroxide, **74**
    preparation, 74
    properties, 75
    tests for, 76
Hydrogen sulfide, 169
    chemical properties, 170
    physical properties, 170
    preparation, 170
    uses in analysis, 172
Hydrone, 46
Hydroxides, preparation of, 368
Hydroxylamine, 231
Hypo, 187, 381
Hypobromous acid, 135
Hypochlorous acid, **127**, 130
Hypoiodous acid, 135

Ice plant, 228
Indicators, 157
Indigo, 475
Indium, 480
Inks, 536
Iodic acid, 135
Iodine, 118
Ionic equilibrium, 418
Ionic theory, 142
Ionization, **137**
    and conductivity, **147**
    percentage of, 148
    proof of, 137
Iridium, 547
Iron, 525
    metallurgy, 526
    occurrence, 525
    properties, 535
    tests for, 539
Isomerism, 319
Isomorphism, 167, 267
Isotropes, 507

Javelle water, 127, 130

Kaolin, 476
Ketones, 320
Kiln, 399
Kinetic theory of gases, 38
Krypton, 216

Lactic acid, 321
Lampblack, 283

- LANE, 201
- Laughing gas, 236
- LAVOISIER, 13, 20, 44
- Law of BOYLE, 33
  - CHARLES', 35
  - definite composition, 4
  - DULONG and PETIT, 85
  - GAY-LUSSAC, 52
  - GRAHAM, 37
  - HENRY'S, 91
  - multiple proportions, 7
  - partial pressures, 37
  - partition, 93
- Lead, 487
  - acetate, 492
  - bromide, 492
  - chamber process, 180
  - chloride, 492
  - chromate, 492
  - dioxide, 490
  - iodide, 492
  - metallurgy, 487
  - monoxide, 490
  - nitrate, 492
  - occurrence, 487
  - oxides, 489
  - pencils, 279
  - poisoning, 489
  - properties, 488
  - refining, 488
  - sulfate, 492
  - sulfide, 492
  - tetrachloride, 491
  - tree, 488
- LE BLANC process, 377
- LE CHATELIER'S principle, 224, 415, 416
- Legumes, 221
- Levulose, 327
- Lignite, 281
- Lime-sulfur, 174
- Liquefaction of gases, 213
- Liquid air, 211
- Litharge, 490
- Lithium, 371
- Lithopone, 450
- Luminosity, 311
- Luminous paint, 403

- Magnalium, 275
- Magnesia mixture, 444
- Magnesium, 441
  - ammonium phosphate, 494
  - carbonate, 443
  - chloride, 443
  - hydroxide, 443
  - nitride, 442
  - occurrence, 441
  - oxide, 442
  - preparation, 442
  - sulfate, 444
- Malt, 329
- Maltase, 329
- Maltose, 327, 329
- Manganese, 518
  - compounds, 523
  - dioxide, 523
  - metallurgy, 519
  - occurrence, 519
  - properties, 519
  - salts, 519
  - steel, 534
  - tests for, 524
  - tetrachloride, 104
- Manganic compounds, 523
- Manganous compounds, 523
- Marble, 398
- Marsh test, 264, 272
- Mass action, 416
- Matches, 253
- Matter, 1
- MEKER burner, 312
- Melting point, 42
- MENDELEEF, 193
- Mercury, 452
  - complex compounds of, 457
  - fulminate, 457
  - metallurgy, 452
  - occurrence, 452
  - properties, 453
  - purification, 453
  - tests for, 457
- Mercuric chloride, 455
  - compounds, 455
  - cyanide, 456
  - iodide, 456
  - nitrate, 456
  - oxide, 455
  - sulfide, 456
  - thiocyanate, 457
- Mercurous compounds, 454
  - chloride, 454
  - nitrate, 455
  - oxide, 454
- Mesothorium, 509
- Metals, chemical properties of, 363
  - definition of, 19, 67
  - extraction from ores, 364
  - occurrence, 363
  - physical properties, 361
  - preparation of compounds of, 365
- Metantimonic acid, 272
- Metaphosphoric acid, 257
- Metastannic acid, 486
- Methane, 296
  - series, 295
- Methyl alcohol, 314, 317
  - group, 314
- MEYER, 193
- Microcosmic salt, 258
- Microphotographs, 535
- MILLIKAN, 10
- Minium, 491
- Mirrors, 435
- Misch metal, 479
- MITCHERLICH'S law, 267
- MOISSAN, 118, 278
- Molecular and atomic weights, 78
- Molecules, definition of, 9
- Molybdenum, 499, 534
  - sulfide, 499
  - trioxide, 499
- Molybdic acid, 499
- Monazite sand, 479
- Monel metal, 541
- Monosodium phosphate, 258
- Mordants, 475
- MORLEY, 52
- MORSE, 100

- Mortar, 401
- Moseley, 202
- Muscle Shoals, 225

- Naphtha, 301
- Nascent state, 49, 235
- Nelson cell, 375, 376
- Neon, 216
- Nessler's solution, 456
- Neutralization, 155
- Newland's octaves, 193
- Nichrome, 275
- Nickel, 541
    - carbonate, 542
    - chloride, 542
    - compounds, 542
    - nitrate, 542
    - occurrence, 541
    - preparation, 541
    - properties, 541
    - sulfate, 542
    - tests for, 543
- Niton, 506
- Nitrates and nitrites, 241
- Nitric acid, 233
    - action on non-metals, 235
        - metals, 235
        - metallic oxides, 235
        - organic compounds, 235
- Nitric oxide, 236
- Nitrobenzene, 303
- Nitrogen, **217**
    - chemical properties, 219
    - cycle in nature, 220
    - occurrence, 217
    - physical properties, 219
    - pentoxide, 239
    - peroxide, 237
    - preparation, 218
    - trioxide, 238
    - uses, 221
- Nitroglycerine, 245
- Nitrous acid, 241
    - oxide, 236

- Oildag, 279
- Oil gas, 310
    - shales, 223
- Old Dutch process, 493
- Olein, 322
- Oleomargarine, 322
- Onnes, 213, 214
- Open-hearth process, 533
- Orthoantimonic acid, 271
- Orthophosphoric acid, 255, **256**
- Osmium, 547
- Osmosis, 98
- Osmotic pressure, 97
- Ostwald, 142
    - process, 240
- Oxalic acid, 321
- Oxidation, 22, 243
    - and reduction, 464
        - of chromium compounds, 511, 514
        - of manganese compounds, 520, 522
- Oxides, 365, 19
    - of nitrogen, 236
- Oxidizing and reducing flames, 313
- Oxygen, **13**
    - carbon-dioxide balance, 206
    - chemical properties, 17
    - occurrence, 14
    - physical properties, 17
    - preparation, 14
    - tree, 25
    - uses, 24
- Ozone, **27**
    - occurrence, 27
    - preparation, 27
    - properties, 28
    - tests for, 31
    - uses, 30

- Paint, 493
    - drying of, 23
- Palladium, 546
- Palmitin, 322
- Paper making, 324
- Parkes process, 434
- Passive metals, 511
- Pectin, 357
- Perchloric acid, 134
- Periodic system, 192
    - table, 194
- Permutit process, 407
- Peroxides, 76
- Persulfuric acid, 187
- Petroleum, 299
- Pewter, 276
- Phenol, 303
- Phlogiston, 20
- Phosgene, 290
- Phosphate fertilizers, 263
    - rock, 251, 263
    - tests for, 263
- Phosphides, 263
- Phosphine, 261
- Phosphoric acid, ionization of, 259
- Phosphorous acid, 255
- Phosphorus, 251
    - occurrence, 251
    - pentachloride, 254
    - pentoxide, 261
    - preparation, 252
    - properties, 252
    - red, 253
    - sulfides, 263
    - trichloride, 254
    - white, 253
- Photography, 436
- Physical change, 4
- Picric acid, 246, 303
- Pig iron, 530
- Pintsch gas, 310
- Pitchblende, 502
- Plaster of paris, 401
- Platinic chloride, 546
- Platinum, 544
    - chloride, 545
    - compounds, 545
    - sponge, 545
- Poison gas, 111
- Polysulfides, 173, 393
- Porcelain, 476
- Portland cement, 477
- Potassium, 385
    - bromide, 387

Potassium carbonate, 388
    chlorate, 133, 388
    chloride, 387
    chloroplatinate, 391
    cyanide, 389
    hydroxide, 388
    nitrate, 389
    occurrence, 385
    perchlorate, 391
    permanganate, 522
    preparation, 386
    properties, 387
    pyroantimonate, 272
    sulfate, 389
    sulfide, 390
    tests for, 290
Pottery, 476
Precipitation conditions, 421
Priestley, 13, 20, 221, 236
Producer gas, 309
Protein, 330, 357
Prussic acid, 293, 382
Pyrephoric iron, 536
Pyrone fire extinguisher, 291
Pyrophosphoric acid, 257
Pyrosulfates, 187
Pyroxylin, 247

Quartz, 338
Quicklime, 398

Radioactivity, 502
Radiolite watch faces, 508
Radium, 504
    emanation, 506
    energy, 507
    industry, 508
    uses, 508
Ramsay, 214, 216, 506
Raoult, 96
Rare earths, 478
Rayleigh, 214
Red lead, 491
Reduction, 53, 243
Reverberatory furnaces, 425
Reversible reactions, 53
Review suggestions, 32, 58
Rhodium, 546
Richards, 84
Röntgen, 503
Rose's metal, 274
Rubidium, 393, 394
Ruthenium, 547
Rutile, 495

Safety lamp, 312
Sal soda, 376
Salt cake, 409
Salts, methods of preparation, 151, 152, 366
    solubility of, 368
Saponification, 323
Scheele, 13, 103, 169
Selenium, 189, **190**
Serpek process, 225
Sherardizing, 447
Shoop process, 447
Siemens regenerative process, 533
Silica, 338
    gel, 338
Silicates, 340
Silicic acid, 337
Silicides, 337
Silicol process, 47
Silicon, 336
    occurrence, 336
    preparation, 336
    properties, 337
    tetrachloride, 337
    tetrafluoride, 126, 339
Silk, 247
    artificial, 325
Silver, 433
    carbonate, 437
    chromate, 437
    chloride, 435
    cyanide, 437
    halides, 435
    metallurgy, 433
    nitrate, 437
    occurrence, 433
    oxide, 435
    phosphate, 437
    properties, 434
    sulfate, 437
    uses, 435
Slosson, 335
Smokeless powder, 246
Soaps, **323**, 358
Soda, 376
Sodamide, 227
Sodium, 371
    amalgam, 373
    bicarbonate, 379
    bisulfate, 380
    bromide, 373
    carbonate, 376
    chloride, 373
    fluoride, 374
    hydroxide, 374
    hydrosulfite, 188
    iodide, 373
    nitrate, 383
    nitrite, 241
    occurrence, 371
    peroxide, 17
    preparation, 371
    properties, 372
    stannite, 484
    sulfate, 380
    sulfide, 382
    sulfite, 381
    thiosulfate, 381
Softening water, 406
Soil fertility, 231
Solder, 274, 276
Solubility curves, 90
    of gases in liquids, 91
    liquids in liquids, 91
    measuring, 88
    of mixed gases, 92
Solubility product, 421
Solute, 87
Solutions, **86**
    molar, 94
    normal, 94
    saturated, 88
    supersaturated, 87, 88
Solution pressure, 462
Solvay process, 378

Solvent, 87
Solving problems, 57
Specific heat, 66, 85
Spectra, dark line, 395
Spectroscope, 394
Speed of reactions, 26
Spinels, 472
Spinthariscope, 505
Standard solutions, 156
Stannic compounds, 485
    acid, 486
    chloride, 485
    sulfide, 487
Stannous compounds, 483
    chloride, 484
    hydroxide, 484
    oxide, 484
    sulfide, 484
Starch, 326
Stassfurt deposits, 103, 373, 385
Stearin, 322
Steel, 531
Stellite, 276
Stibine, 272
Storage battery, 493
Stove polish, 279
Strength of acids and bases, 148
Strontium, 411
    hydroxide, 412
    nitrate, 411
    occurrence, 411
Sucrose, 327
Sugars, 326
    beet, 327
    cane, 327
    invert, 327
    maple, 327
Sugar of lead, 492
Sulfates, 187
Sulfites, 179
Sulfo acids and salts, 268, 272, 484
Sulfur, 161
    chemical properties, 168
    dioxide, 175
        chemical properties, 178
        physical properties, 177
        preparation, 175
        uses, 178
    occurrence, 161
    physical properties, 162
    trioxide, 180
    uses, 168
Sulfuric acid, 180
    properties, 185
    uses, 186
Sulfurous acid, 178
Superphosphate, 403
Suspensoids, 354
Sylvite, 385

Talc, 441
Tantalum, 498
Tartar emetic, 271
Tartaric acid, 321
Tellurium, 189, **191**
Thallium, 480
Thermos bottles, 212
Thiosulfuric acid, 187
Thorium, 496, 509
Three states of matter, 42
Tin, 481
    metallurgy, 482
    occurrence, 481
    properties, 482
    tests, 487
Titanium, 495
Titration, 156
T. N. T., 245
Toluene, 304
Transition points, 90
Trinitrotoluene, 245
Trisodium phosphate, 257
Tungsten, 500
    compounds, 501
    lamps, 501
    steel, 534
Type metal, 276

Ultramarine, 477
Ultraviolet light, 395
Uranium, 502
Urea, 291

Valence, 59
Vanadium, 497, 534
VAN'T HOFF, 101
Vapor tension, 68
Vaseline, 301
Ventilation, 209
Vinegar, 320
Viscose, 326
Vitamines, 331
Vitriols, 187, 430

Water, **65**
    boiling point, 69
    chemical properties, 66
    natural, 70
    of crystallization, 68
    physical properties, 65
    purification, 71
Water gas, 307
    glass, 339
WATT, 464
Welsbach gas mantles, 312, 479
Whiskey, 329
White lead, 493
WILSON, 292
WÖHLER, 294
Wood alcohol, 317
WOODHOUSE, 386, 387
WOODS' metal, 274
Wrought iron, 531

Xenon, 216
X-rays, 503
X-ray spectra, 201

Zeppelins, 56
Zinc, 444
    chart, 451
    chloride, 449
    hydroxide, 447
    metallurgy, 445
    occurrence, 444
    properties, 446
    sulfide, 449
    tests for, 450
    uses, 446
Zirconium, 495
Zymase, 328

Date Due

540.H75G
a39001 006991411b

H75g

65-1
69-1

77-1
74